Analytical and Sensory Differentiation of 1-Octen-3-ol Enantiomers

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The enantiomers of 1-octen-3-ol were synthesized by reductive cleavage of various corresponding optically pure diastereomeric esters. Absolute configurations were correlated with ^{1}H NMR spectroscopic behavior of diastereomeric esters of (*S*)-(+)-*O*-acetylmandelic acid (1), (*R*)-(−)-α-phenylpropionic acid (2), (*R*)-(+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetic acid (3), and (*S*)-(−)-α-methoxy-α-[(trifluoromethyl)phenyl]acetic acid (4). Sensory tests carried out with (*R*)-(−)-1-octen-3-ol and (*S*)-(+)-1-octen-3-ol showed that the characteristic mushroomlike odor is exclusively caused by the (*R*)-(−) antipode.

The influence of chirality to odor quality is well-known for a number of aroma components (Russel and Hills, 1971; Friedman and Miller, 1971; Ohloff and Giersch, 1980; Mosandl and Heusinger, 1984, 1985a,b). Therefore, our aim of research on structure–function relationship of flavor compounds is (i) to study the sensory and physiological properties of enantiomers and (ii) to check the optical purity in order to identify racemic mixtures and to control asymmetric syntheses by chemical or biotechnological methods. The present study is devoted to the enantiomers of 1-octen-3-ol. The levorotatory antipode, formed by enzymic oxidative breakdown of linoleic acid (Wurzenberger and Grosch, 1982, 1983, 1984; Grosch and Wurzenberger, 1985) has been described as character impact flavor compound of mushrooms (Freytag and Ney, 1968, 1969; Tressl et al., 1980). But the final determination of configuration of the 1-octen-3-ol enantiomers by spectroscopic methods has not been provided as yet. Furthermore, the sensory properties of both optically pure antipodes are not described.

EXPERIMENTAL SECTION

Materials. Optically pure (*R*)-(−)-phenylpropionic acid (2) and (*S*)-(+)-*O*-acetylmandelic acid (1) were synthesized, according to the literature (Helmchen, 1976; Staiger, 1980). (±)-1-Octen-3-ol, (*R*)-(+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetic acid (3), and (*S*)-(−)-α-methoxy-α-[(trifluoromethyl)phenyl]acetic acid (4) were purchased from Aldrich.

Gas–Liquid Chromatography. A Hewlett-Packard 5830A gas chromatograph with FID equipped with a fused silica column (SE 54, 25 m, 0.32 mm i.d.) was used; for conditions see Synthesis and Separation of Compounds.

Gas–Liquid Chromatography–Mass Spectrometry. A Pye Unicam gas chromatograph coupled to a LKB 2091 mass spectrometer was available. The apparatus was equipped with a fused silica column (SE 54, 25 m, 0.32 mm i.d.). Conditions: ion source temperature, 260 °C; electron energy, 70 eV.

NMR Spectral Analyses. ^{1}H NMR spectra were recorded on JEOL C-60 HL (60-MHz) and a Bruker WM 400 (400-MHz) instruments, respectively. Samples were run in C_6D_6 with Me_4Si as internal standard.

IR Spectral Analyses. The IR spectra were measured as a smear on sodium chloride plates with a Beckman IR 4240 spectrophotometer.

Liquid Chromatography. Apparatus: Gilson, Model 303 with Gilson Holochrome UV/vis detector (190–600 nm); syringe loading sample injector, Model 7125 (Rheodyne).

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SYNTHESIS AND SEPARATION OF COMPOUNDS

(1) (*S*)-*O*-Acetylmandelic Acid 1-Octen-3-yl Ester (A-I, A-II). A 2 mol equiv portion of (*S*)-mandelic acid was transferred to (*S*)-O-acetylmandelic acid (1) with acetyl chloride (60 min, 60 °C) and to acid chloride with thionyl chloride (2 h, 82 °C). To 2 mol equiv of acid chloride in CCl_4 was added 2 mol equiv of (dimethylamino)pyridine (DMAP) in N_2 atmosphere under stirring, and 1 mol equiv of (*R,S*)-1-octen-3-ol was added. Conditions: temperature 1 h, 50 °C; following 15 h at 20 °C, quantitative reaction. Workup conditions: addition of water, extraction with diethyl ether, washing organic layer with 0.5 N KOH and water, drying with Na_2SO_4, chromatographic purification on SiO_2 (63–200 μm). Eluent: pentane/diethyl ether (95:5).

LC Separation (See Figure 1): column, SiO_2, 15–25 μm, Merck; flow, 50 mL/min; eluent, petroleum ether/ethyl acetate (98:2), detection 254 nm; retention times, **A-I** = 46.5 min, **A-II** = 54.5 min; resolution, R = 1.5.

HRGC Behavior: no resolution with SE 54.

Reductive Cleavage: Optically pure diastereomer **A-I (A-II)** was reduced with an excess of $LiAlH_4$ in absolute ether, quantitatively within 20 min at 40 °C to the enantiomers of 1-octen-3-ol; after the addition of water and HCl, it was extracted with ether and purified on silica gel (63–200 μm). Eluent: pentane/ether (95:5). Peak I: (*S*)-(+)-1-octen-3-ol, $[\alpha]^{20}_D$ = +20.6 (*c* 5.3; C_2H_5OH). Peak II: (R)-(−)-1-octen-3-ol, $[\alpha]^{20}_D$ = −20.2 (*c* 7.3; C_2H_5OH).

(2) (*R*)-(−)-α-Phenylpropionic Acid 1-Octen-3-yl Ester (B-I, B-II). A 3 mol equiv portion of **2** was transferred to the corresponding acid chloride with oxalyl chloride (40 min, 30 °C) and reacted at once with 1 mol equiv of 1-octen-3-ol solution in CCl_4 *without* any catalyst in N_2 atmosphere (55 °C, 2 days). After the solvent CCl_4 was reduced to 5 mL, 10 mL of dioxane/H_2O (1:1) was added under stirring for 2 h, the mixture was extracted from 1 N KOH media with benzene/ether (3:7) and washed with 1 N HCl and H_2O, and the organic layer was dried with Na_2SO_4. Conditions: purification by LC on silica gel (65–200 μm); eluent, pentane/ether (94:6); detection, 220 nm.

LC Separation (See Figure 1): column, SiO_2, 15–25 μm, Merck; eluent, pentane/ether (99:1); flow, 30 mL/min; detection, 220 nm; fractionating and HRGC control, SE 54 (25-m) fused silica column.

HRGC Conditions: 50 °C, 2 min isothermal, 5°/min to 200 °C; retention times, **B-I** = 21.3 min, **B-II** = 21.9 min; resolution, R = 1.5; 130 °C isothermal, R = 1.85, α = 1.10.

(3) (*R*)-(+)- and (*S*)-(−)-α-Methoxy-α-[(trifluoromethyl)phenyl]acetic Acid 1-Octen-3-yl Esters C and D. A 2 mol equiv portion of **3** or **4** was transferred to acid chloride (60 h, 82 °C), acid chloride was added to dry pyridine (5 mL) and CCl_4 (5 mL), and 2 mol equiv of

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Table I. ^{1}H NMR Chemical Shifts of the 1-Octen-3-ol Moiety in the Optically Pure Diastereomeric Esters A–D, Isolated by Preparative LC (δ Values, 400 MHz, C_6D_6, Internal Me_4Si)[a]

	1	1′	2	3	4		5,6,7	8
A-I	4.86	4.81	5.47	5.37	1.55	1.43	1.36–1.05	0.85
A-II	5.29	5.01	5.65	5.34	1.41	1.30	1.14–0.87	0.75
B-I	5.17	4.99	5.68	5.36	1.45	1.36	1.15–0.96	0.79
B-II	4.98	4.87	5.54	5.38	1.52	1.42	1.32–1.08	0.83
C,D-I	5.19	4.97	5.59	5.45	1.49	1.35	1.17–0.96	0.79
C,D-II	5.12	4.94	5.50	5.41	1.52	1.38	1.28–1.00	0.82

[a] Coupling constants (^{1}H NMR): $J_{1,2}$ = 17.5 Hz; $J_{1,1'}$ = 1.5 Hz; $J_{1,3}$ = 1.5 Hz; $J_{1',2}$ = 10.75 Hz; $J_{1',3}$ = 1.5 Hz; $J_{1',1}$ = 1.5 Hz.

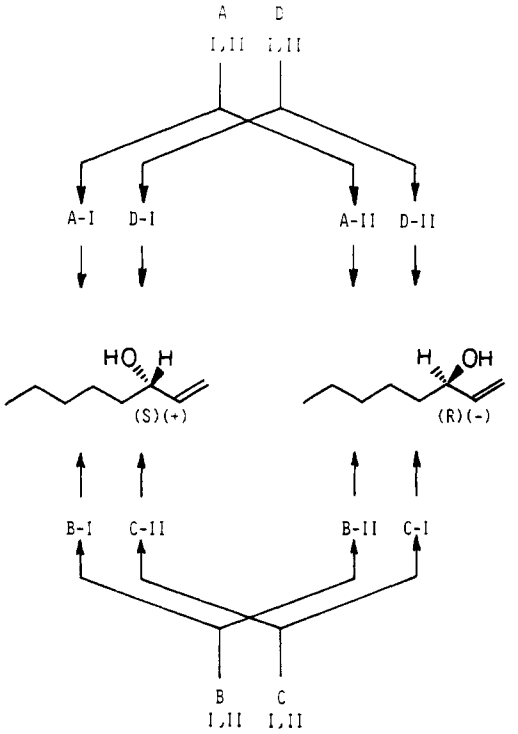
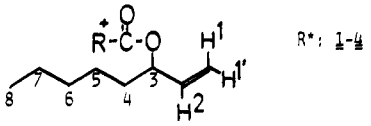


Figure 1. LC separation of diastereomeric esters **A–D** (conditions: cf. Experimental Section).

(*R,S*)-1-octen-3-ol were dropped in. Reaction time: 1 week at 20 °C, quantitative reaction. Before isolation of reaction products, the solution was diluted with water and extracted with ether and the organic layers were combined, washed with 2 N HCl and water, and dried with Na_2SO_4. LC purification: silica gel, 63–200 μm, Merck; eluent, pentane/ether (95:5).

(4) LC Separation of Diastereomers C-I/II and D-I/II. Conditions: see those for **B-I** and **B-II**; HRGC control, SE 54 (25-m) fused silica column; HRGC conditions, 130 °C isothermal; retention times, **C-I (D-I)** = 12.75 min, **C-II (D-II)** = 13.32 min; resolution, R = 1.4. (Note: **C-I (D-I)** and **C-II (D-II)** are enantiomers; therefore, identical retention times on achiral phase—see Figure 2).

Reductive cleavage with $LiAlH_4$ was analogous to reductive cleavage of **A-I** and **A-II**. **C-I (D-II)** yielded (*R*)-(−)-1-octen-3-ol; **C-II (D-I)** yielded (*S*)-(+)-1-octen-3-ol (see Figure 2 and Table I).



(5) Optical Purity Control. Optical purity of 1-octen-3-ol enantiomers, obtained by reductive cleavage of the separated diastereomeric esters (**A–D**), was determined by reesterification with **3**, analogously to the above-mentioned procedure for racemic 1-octen-3-ol. This method proves optical purities higher than 99.9%.

(6) Sensory Description. It was carried out by a panel of experts. For evaluation of sensoric characteristics we are indebted to Messrs. Dragoco Gerberding & Co., GmbH, 3450 Holzminden, FRG. who smelled and tasted solutions of 1-octen-3-ol enantiomers (ethanolic solutions (1%) for evaluation of odor and 10 ppm amounts each in aqueous sucrose for description of taste).

(*R*)-(−)-*1-Octen-3-ol*: intensive mushroomlike, fruity soft odor; taste in accordance with genuine mushroom aroma.

(*S*)-(+)-*1-Octen-3-ol*: odor, herbaceous, some reminscence to mushrooms, but less intensive and not so characteristic in comparison to the (*R*)-(−) antipode; taste, unpleasant, artificial, weak mushroom note.

RESULTS AND DISCUSSION

Analytical information about 1-octen-3-yl esters of **A–D** can be taken from IR and mass spectra.

A: IR (KBr) 3100–3020, 2960, 2930, 2865, 2860, 1750, 1490, 1455, 1450, 1370, 1270, 1255, 1230, 1210, 1175, 1080, 1050, 980, 960, 920, 735, 690 cm^{-1}; mass spectrum, m/z (relative intensity) 150 (4), 149 (32), 118 (5), 108 (6), 107 (82), 105 (20), 90 (12), 89 (9), 79 (25), 78 (5), 77 (23), 69 (20), 67 (9), 57 (6), 55 (22), 54 (11), 53 (11), 52 (4), 51 (7),

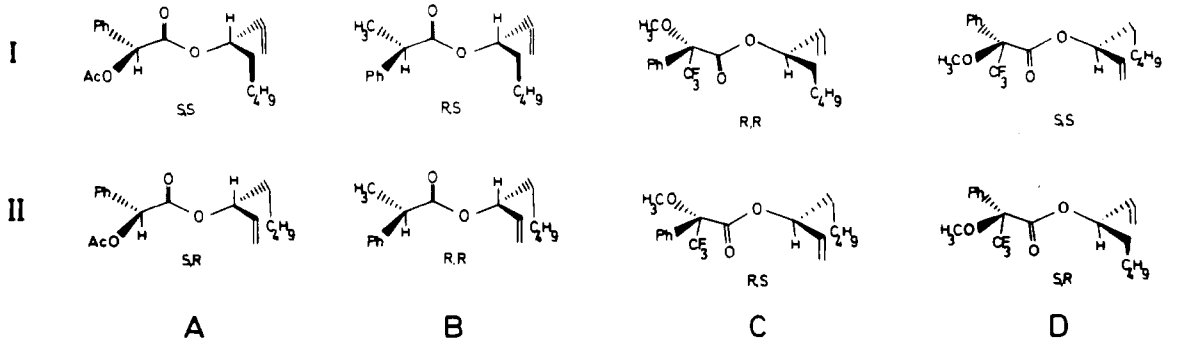


Figure 2. Diastereomeric esters of the chiral acids 1–4 with 1-octen-3-ol, referring to the models of Helmchen (**A, B**) (19) and Mosher (**C, D**) (20), respectively. Conditions: LC behavior on silica; eluent, cf. Experimental Section; order of elution, first (I) and second (II) peak.

Table II. ^{13}C NMR Chemical Shifts of the 1-Octen-3-ol Moiety in the Optically Pure Diastereomeric Esters A–D, Isolated by Preparative LC (δ Values, 100 MHz, C_6D_6, Internal Me_4Si)

	C-1 (t)	C-2 (d)	C-3 (d)	C-4 (t)	C-5 (t)	C-6 (t)	C-7 (t)	C-8 (q)
A-I	116.2	136.3	75.2	34.5	24.9	31.8	22.8	14.2
A-II	116.6	136.3	75.2	34.2	24.6	31.6	22.7	14.0
B-I	116.1	137.3	46.1	34.4	24.7	31.7	22.7	14.0
B-II	115.9	136.9	46.2	34.6	25.1	31.8	22.9	14.2
C,D-I	117.2	134.9	76.4	33.2	23.6	30.6	21.7	13.0
C,D-II	116.8	134.6	76.5	33.3	23.9	30.7	21.7	13.1

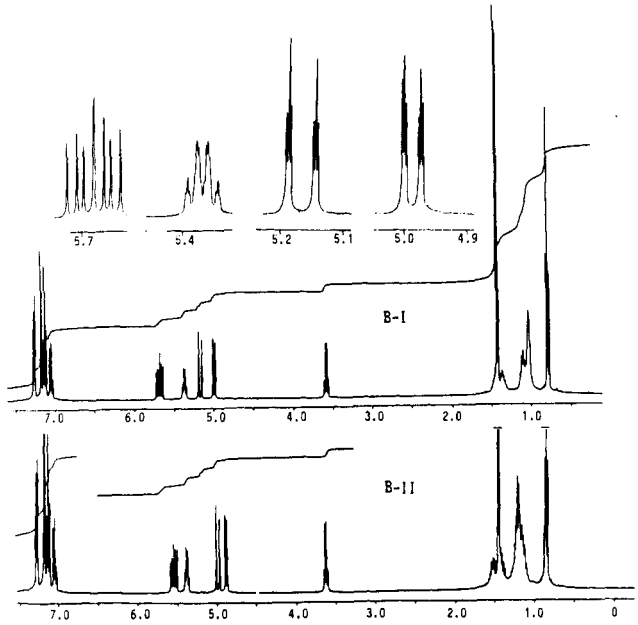


Figure 3. ^1H NMR spectra of the diastereomeric esters **B-I** and **B-II** (400 MHz; C_6D_6, internal Me_4Si).

44 (5), 43 (100), 42 (8), 41 (39), 40 (4).

B: IR (KBr) 3100–2860, 1730, 1490, 1460, 1450, 1370, 1310, 1240, 1195, 1160, 1090, 1070, 1050, 1030, 980, 920, 760, 730, 690 cm^{-1}; mass spectrum, m/z (relative intensity), 260 (M^+, 1), 106 (9), 105 (100), 104 (4), 103 (6), 79 (8), 78 (4), 77 (9), 69 (18), 55 (7), 54 (4), 43 (7), 41 (14).

C (D): IR (KBr) 3100–2860, 1750, 1500, 1470, 1455, 1290, 1270, 1260, 1185, 1170, 1125, 1110, 1080, 1020, 995, 940, 930, 890, 765, 720, 700 cm^{-1}; mass spectrum, m/z (relative intensity) 190 (4), 189 (100), 141 (4), 139 (4), 119 (11), 111 (6), 105 (20), 91 (5), 77 (16), 69 (44), 67 (7), 57 (5), 55 (25), 54 (9), 43 (8), 41 (26).

The corresponding NMR data and spectra are outlined in Tables I and II and Figure 3

Gas chromatographic resolution of 1-octen-3-ol via diastereomeric esters of **3**, recently reported by Tressl et al. (1984, 1985) and Hall et al. (1984), demonstrated the possibility for analytical determination of enantiomeric composition of this chiral component. Although systematic studies of the mechanism of gas–liquid chromatographic separation of diastereomeric esters showed that preferred conformations of groups attached to the asymmetric centers play a key role in separation, a generalization of chromatographic behavior is not warranted (Gil-Av 1974; Karger et al., 1967). The order of elution may be converted within a series of homologues of diastereomeric esters (Hammarström et al., 1973).

In this work absolute configurations of 1-octen-3-ol enantiomers were elucidated by $^1H\{^{13}C\}$ NMR behavior of their optically pure diastereomeric esters (**A–D**), referring to the models of Helmchen (1976) **A-I, A-II, B-I, B-II**) and Dale and Mosher (1973) (**C-I, C-II, D-I, D-II**) (cf. Figure 2 and Table I). These methods are well established and based on chemical shift differences for protons with equivalent constitution. In both models different shifts for comparable groups result from the upfield shift caused by the phenyl ring of the acid moiety. ^1H NMR spectral data and chromatographic behavior (LC, HRGC) of diastereomeric 1-octen-3-yl esters in connection with their reductive cleavage prove unambiguously the (*R*)-(−) and (*S*)-(+) configuration for the enantiomers of 1-octen-3-ol, which are very different in their sensory properties.

For sensory evaluation of 1-octen-3-ol enantiomers, some indications are reported by Dijkstra and Wikén (1976). But generation of highly optically pure enantiomers in preparative scale was needed as a prerequisite for reliable sensory differentiation: (*R*)-(−)-1-octen-3-ol was found to be exclusively responsible for the fruity, mushroomlike flavor, while the (*S*)-(+) antipode exhibits a moldy grassy note.

ACKNOWLEDGMENT

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Registry No. **1**, 7322-88-5; **2**, 7782-26-5; **3**, 20445-31-2; **4**, 17257-71-5; A-I, 99618-80-1; A-II, 99618-84-5; B-I, 99618-81-2; B-II, 99618-85-6; C-I, 99618-82-3; C-II, 99618-86-7; D-I, 99618-83-4; D-II, 99618-87-8; (*R*)-CH_2=CHCH(OH)$(CH_2)_4$Me, 3687-48-7; (*S*)-CH_2=CHCH(OH)$(CH_2)_4$Me, 24587-53-9; (*S*)-PhCH(OH)CO_2H, 17199-29-0; (±)-CH_2=CHCH(OH)$(CH_2)_4$Me, 50999-79-6.

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Sucrose in Methanolic Calcium Chloride

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The solubility of sucrose in methanolic calcium chloride solution and the effect of various parameters were studied. The solubility of sucrose in methanol containing 30% $CaCl_2$ (w/v) was 45% (w/v) at 68 °C. Addition of acetone to the system recovered approximately 90% of the sucrose as a precipitate. Precipitation with phosphoric acid removed most of the calcium as tricalcium phosphate, leaving sucrose in solution. Methanolic NaOH precipitated both the sucrose and calcium in methanol, while with aqueous NaOH formation of the sucrose–$Ca(OH)_2$ complex depended on the concentration of the reactants.

Complexes of carbohydrates with alkali and alkaline-earth metal salts and bases in aqueous solution have been extensively studied (Jensen et al., 1940; Rendleman, 1966a; Roy and Mitra, 1972; Moulik and Mitra, 1973; Moulik and Khan, 1975). The interaction of CaO with sucrose has long been utilized in the Steffen process in the beet sugar industry (McGinnis, 1982). Similar procedures have been the subject of extensive investigations in the dairy industry in efforts to recover lactose from cheese whey (Cerbulis, 1973; Nickerson, 1979; McCommins et al., 1980; Quickert and Bernhard, 1982). However, investigations of alkali-metal complexes of carbohydrates in alcoholic solutions are rare, except for the comprehensive study by Rendleman (1966b,c) on the interaction, in ethanol, of a series of sodium and potassium salts and bases with carbohydrates and their derivatives. In previous studies of nonaqueous solvents for carbohydrates, methanol has received little attention due to its relatively low solvent power (less than 1% for sucrose) (Moye, 1972). Domovs and Freund (1960) observed increased solubility for a wide range of carbohydrates in methanol containing calcium chloride, described a heptahydrate complex of lactose–calcium chloride in the presence of water, and obtained a crystalline lactose–$CaCl_2$–$4CH_3OH$ under anhydrous condition. A sodium hydroxide complex of sucrose has been isolated from methanolic media by Rendleman (1966c).

The objectives of the present study were to (1) determine the effects of various parameters such as temperature and concentration on the solubility of sucrose in methanolic calcium chloride solution and (2) investigate possible methods to recover the sucrose from the system.

EXPERIMENTAL PROCEDURES

Determination of Solubility. Methanolic calcium chloride stock solution was prepared by saturating methanol (0.02% moisture) with anhydrous $CaCl_2$ by shaking for 1 h at 60 °C. Solutions of various concentrations of calcium chloride were then prepared by diluting the stock solution. All experiments were done in capped 25-mL vials. The solubility of sucrose in methanol at various concentrations of $CaCl_2$ was determined by adding sufficient sucrose to always form an equilibrium of saturated sucrose solution and sucrose crystals at a given temperature and time of mixing.

Precipitation of Sucrose and Calcium from Solution. Fixed volumes of various concentrations of sodium hydroxide, phosphoric acid, and acetone were added to the methanol solution of sucrose and $CaCl_2$ with rapid mixing, in 12-mL clinical centrifuge tubes. The flocculent precipitate formed was set for 10 min and then centrifuged down. The supernatant was analyzed for sucrose, calcium, and chloride concentrations. A methanolic NaOH solution was prepared and added to the methanolic $CaCl_2$–sucrose solution. Alternatively, the methanolic $CaCl_2$–sucrose solution was evaporated to dryness, before an aqueous solution of NaOH was added. In all recovery experiments, a 4–6% sucrose solution was used. The concentration of sucrose remaining in solution was calculated on the basis of the initial volume of the methanolic $CaCl_2$–sucrose solution used.

Carbohydrate Analysis. The sucrose dissolved in methanolic calcium chloride solution was analyzed by the phenol–H_2SO_4 method described by Dubois et al. (1956). The methanol in the sample did not interfere with the colorimetric determination. In some cases, to detect the decomposition of sucrose, methanol was evaporated and the ferricyanide submicro method was used (Guinn, 1967).

Calcium Determination. Aliquots of sucrose-containing methanolic $CaCl_2$ solution were air-dried before 7.5 mL of hydroxynaphthol blue (HNB) buffer solution (pH 13.0) and 42.5 mL of H_2O were added. The solution was titrated with standardized titraver solution ($^1/_{28}$ N EDTA, pH 5) to a blue end point using 0.1 g HNB as indicator (Zaragosa et al., 1982).

Alternatively, calcium was analyzed by atomic absorption using a Perkin Elmer 303 AA spectrophotometer on samples prepared by dry ashing (Anon 1982).

Chloride Determination. The Mohr method by titrating with $AgNO_3$, using K_2CrO_4 as an indicator, was used (Johnson and Ulrich, 1959). In all the determinations, the methanol was evaporated before analyses.

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