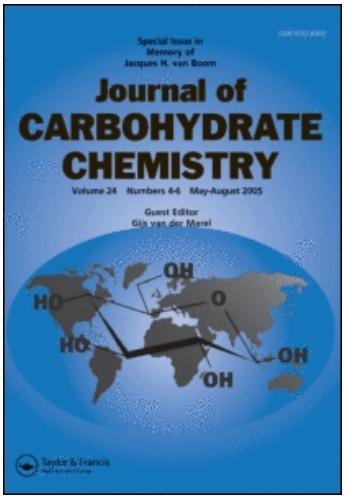


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Monoacetalization of Unprotected Sucrose with Citral And Ionones[1]

Piotr Salanski[a]; Gérard Descotes[a]; Alain Bouchu[a]; Yves Queneau[a]
[a] Unité Mixte de Sucrochimie CNRS - Béghin-Say (UMR 143), Villeurbanne Cedex, France

To cite this Article Salanski, Piotr , Descotes, Gérard , Bouchu, Alain and Queneau, Yves(1998) 'Monoacetalization of Unprotected Sucrose with Citral And Ionones[1]', Journal of Carbohydrate Chemistry, 17: 1, 129 — 142
To link to this Article: DOI: 10.1080/07328309808005773
URL: http://dx.doi.org/10.1080/07328309808005773

J. CARBOHYDRATE CHEMISTRY, 17(1), 129-142 (1998)

MONOACETALIZATION OF UNPROTECTED SUCROSE WITH CITRAL AND IONONES [1]

Piotr Salanski,[2] Gérard Descotes, Alain Bouchu and Yves Queneau*

Unité Mixte de Sucrochimie CNRS - Béghin-Say (UMR 143)
c/o Eridania Béghin-Say, 27 Bd du 11 novembre 1918, B.P. 2132
69603 Villeurbanne Cedex, France

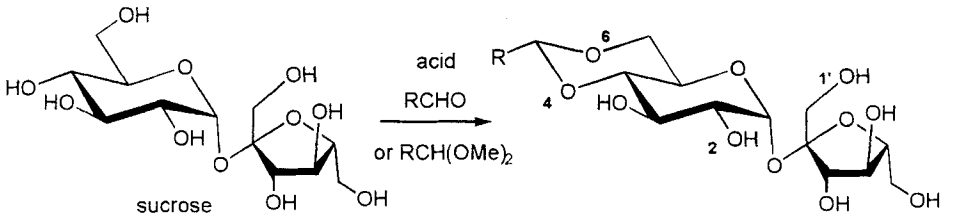
Received April 15, 1997 - Final Form October 21, 1997

ABSTRACT

The monoacetalization of sucrose by citral, α-ionone and β-ionone is reported. Geranial and neral sucrose acetals (*E* and *Z* isomers of citral acetals) are described. Optimization of the acidic catalysis afforded good yields of acetals directly from unprotected sucrose by transacetalization of dimethyl acetals in dimethylformamide. The influence of microwave irradiation on the reaction outcome was investigated.

INTRODUCTION

The chemical utilization of sucrose requires clean and efficient methodologies, but examples of selective chemical transformations of unprotected sucrose are still rather scarce.[3,4] The 1° alcohol functions of sucrose can be reacted selectively over the 2° alcohol functions when steric factors can be taken advantage of. However, reactions often occur unselectively on one or more of the three 1° hydroxyl groups. In terms of acidity, the most reactive hydroxyl group of sucrose is at C-2, on the carbon next to the anomeric carbon of



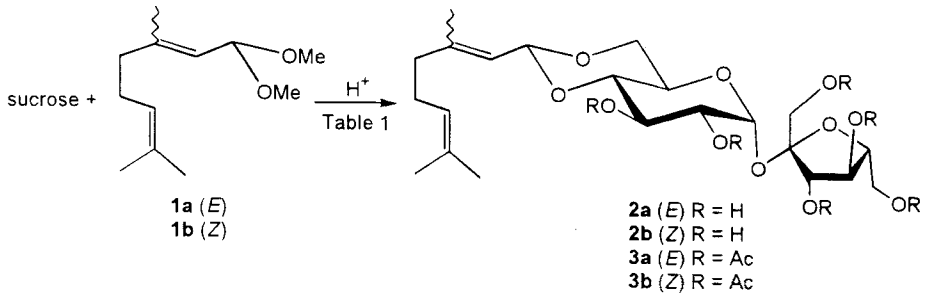
Scheme 1

the glucosyl moiety.[5] The hydroxyl groups on 1' and 3', both on carbons next to the anomeric carbon of the fructosyl moiety, can compete with OH-2 because they are involved in the same hydrogen bonding network.[6,7]

Acetalization at the 4,6-positions of sucrose also provides a potential tool for selectively providing monosubstituted sucrose derivatives because of the unique OH-4 - C-4-5-6 - OH-6 sequence which produces only one six-membered ring acetal linkage having a *trans* decalin-type junction with the glucosyl ring of sucrose (Scheme 1).[8,9] Only when increasing the carbonyl compound quantity and (or) prolonging the reaction time, can further bridge acetalization occur, involving OH-2 and OH-1'.[10]

The preparation of carbohydrate cyclic acetals of this type is well known,[11-17] *e.g.* 4,6-*O*-benzylidene glucose, but the acidic catalysis which is required to achieve the acetalization process is often not compatible with the stability of sucrose or its derivatives. Therefore, milder conditions are required for comparable acetalization reaction using unprotected sucrose. Very recently, Gelas and coworkers[9] reported the synthesis of a series of sucrose long chain acetals, obtained by transacetalation of dimethyl acetals of alkanals to a 4,6-diol sucrose derivative, fully protected on other positions. Transacetalation using unprotected sucrose in DMF was also described, in the special case of α,β-unsaturated aldehydes or ketones dialkyl acetals.[8,9] The use of excess of the carbonyl compound limited the conversion ratio of the more expensive partner of the reaction. This work described the synthesis of a number of sucrose acetals, notably some amphiphilic compounds, for which the critical micellar concentration was measured in order to evaluate their tensioactive properties.

Pursuing efforts to apply this methodology to the chemistry of unprotected sucrose, we investigated more closely the reaction of citral [(*E,Z*)-3,7-dimethyl-octa-2,6-dienal] and α- and β-ionones, which are attractive aldehydes for this investigation as they



Scheme 2

Table 1. Yields of sucrose citral acetals **2ab** for the reaction of CDMA with excess of sucrose (3 eq) in anhydrous DMF (2-3 mL /mmol sucrose) at room temperature, depending on acidic conditions (0.02 eq / CDMA).

acid[a]	*p*-TsOH[b]	*p*-TsOH	PPTS	PyHCl	PVPPTS	PVPPTS[c]	PVPPTS[c]
t (h)	72	17	1.5	4	4	flow	batch
yield (%)	34	68	78	68	51	42	14

a. Py = pyridine, PPTS = pyridinium *p*-toluenesulfonate, PVPPTS = polyvinylpyridinium *p*-toluenesulfonate. b. Excess CDMA : 1.3:1. c. Column or batch reaction using 2.4 eq of PVPPTS / CDMA.

are quite inexpensive and widely used chemical intermediates in the perfume industry.[18] In particular, we sought optimized acidic conditions compatible with sucrose chemical stability.

RESULTS AND DISCUSSION

Acid catalyzed acetalization of sucrose

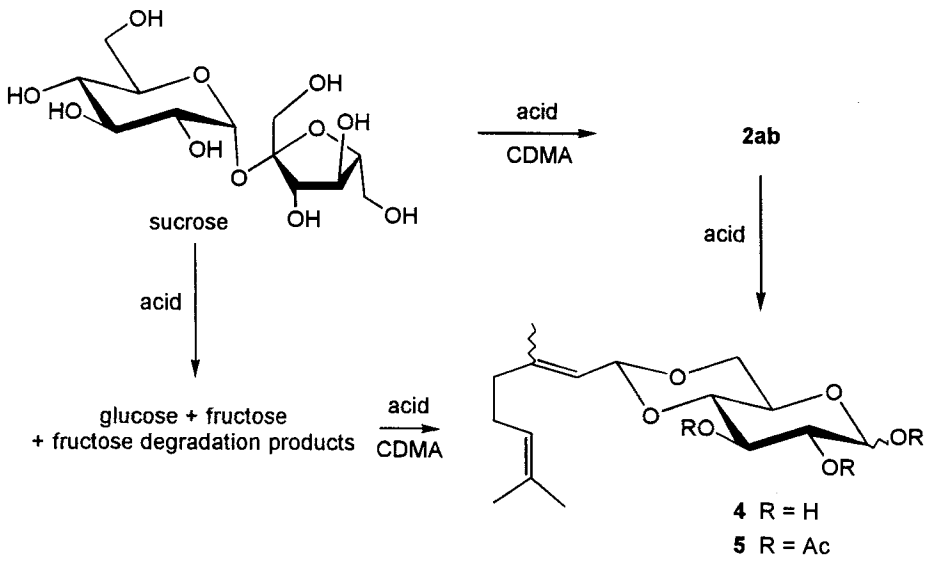
Commercially available citral dimethyl acetal (CDMA, **1ab**) is an *ca.* 2:1 mixture of *E* and *Z* geometric isomers of 3,7-dimethyl-octa-2,6-dienal (geranial and neral). Reaction of **1ab** with excess sucrose (typically 2 to 3 equivalents) in DMF in the presence of an acidic catalyst led to the formation of 4,6-acetals **2ab** (Scheme 2). Specific proof of the regiochemistry was obtained by NMR spectroscopy study (*vide infra*). Using a number of acidic conditions, and in particular soft acids such as sulfonic acid pyridinium salts, good yields of sucrose acetals were obtained (Table 1).

Table 2. Yields of sucrose citral acetals **2ab** for the reaction of CDMA with excess of sucrose (2 eq) in anhydrous DMF (1.5 mL /mmol sucrose) at room temperature, PPTS (0.02 eq / CDMA).

t (min)	20	30	60	90	150
yield (%)	58	63	68	78	66

Preparation of pure geranial sucrose acetal (*E*, **2a**) and neral sucrose acetal (*Z*, **2b**) was attempted by the same method. Starting from geraniol or nerol, geranial and neral were synthesized (Swern oxidation), but it was unfortunately not possible to circumvent the isomerization of the double bond during the acetalization process, even under very mild conditions such as the use of methoxytrimethylsilane with catalytic amounts of trimethylsilyl trifluoromethanesulfonate at -78 °C in dichloromethane. The same 2:1 mixture of *E* and *Z* dimethyl acetals were always obtained.[19,20] Direct reaction of the pure aldehydes with sucrose gave enriched mixtures of sucrose acetals, albeit with low conversion and yield. Geranial, with a faster reaction rate than neral, gave a 6:1 ratio of **2a** and **2b**, allowing full assignment of spectroscopic parameters for both isomers. These enriched mixtures could be further purified by semipreparative HPLC (NH_2 column, acetonitrile-water as eluent), providing pure sucrose geranial and neral acetals which were fully characterized as their peracetylated derivatives **3a** and **3b**.

The best yields of citral sucrose acetals **2ab** are obviously obtained when very mild acidic catalysts are used. Pyridinium *p*-toluenesulfonate (PPTS) appears to be especially efficient, leading to *ca.* 75 % yields of isolated unprotected acetals **2ab** (Table 2). With prolonged reaction time, reverse transacetalation of products or cleavage of the glycosidic bond led to lower yields. The polymeric analog of PPTS, polyvinylpyridinium *p*-toluenesulfonate (PVPPTS) was conveniently used packed in a column, and eluted with a solution of sucrose and CDMA in DMF to give acetals **2ab** in a 44 % yield. A much lower amount (14 %) was obtained using the same quantity of reagents in a batch reaction, leading to significant amounts of glucose acetal **4**. This latter compound can arise either from direct cleavage of sucrose acetals **2ab** or by transacetalation of CDMA by glucose produced by acid catalyzed sucrose cleavage (Scheme 3).



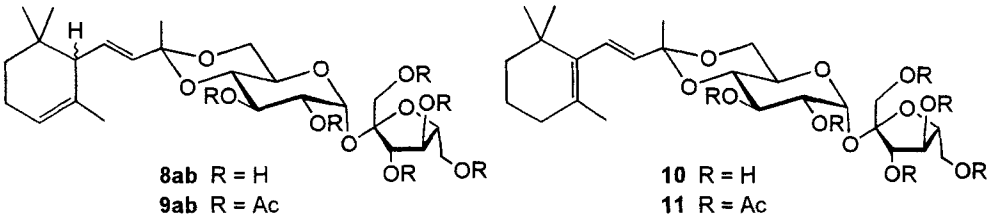
Scheme 3

Table 3. Reaction of citral with excess sucrose (2-3 eq) in DMF, under acidic conditions.

acid	t(h)	yield (%)
PPTS (2 mol %)	20	21
PyHCl (2 mol %)	20	19
PVPPTS (2 mol %)	20	33
PVPPTS (10 mol %)	7	22
PVPPTS (240 mol %)	flow	12

Direct reaction of citral was also investigated. Under standard conditions as employed for performing the reaction from CDMA, a 21 % yield of sucrose acetals **2ab** was obtained, with a low conversion ratio of the aldehyde (*ca.* 35 %). The reaction suffers from the fact that water is not excluded from the system, and the reaction reaches an equilibrium. Increasing the amount of catalyst to 10 mol % in the case of polymeric PVPPTS resulted in a 33 % yield, and using the PVPPTS column to simulate a bench scale flow system, a 12 % yield of **2ab** was obtained (Table 3).

We then turned to α- and β-ionones as carbonyl substrates, in order to evaluate α,β-unsaturated ketones in this reaction. Ionones, like citral, are chemicals of industrial



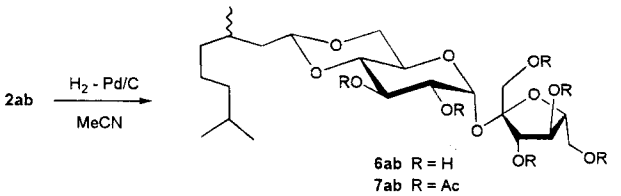
Scheme 4

importance, used as flavouring agents in perfumery. Applying to α- or β-ionone dimethyl acetals the reactions conditions optimized for the citral example, transacetalization of sucrose gave the corresponding sucrose acetals. α-Ionone sucrose acetals **8ab** were thus obtained as a 1:1 mixture of epimers at the cyclohexenyl junction in a 66 % yield, whereas compound **10** was obtained from β-ionone (76 %). These sucrose derivatives were peracetylated (**9ab**, **11**) for characterization purposes (Scheme 4).

Warned by our experience of the neral and geranial isomerization during the ketalization and transketalization reactions, we paid special attention to the double bond geometry in these new sucrose derivatives. However, no trace of *Z* isomers, neither in the α- nor in the β-ionone series, could be detected. This means that starting from β-ionone, a single sucrose derivative is obtained in 75% isolated yield from unprotected sucrose. The assignment of the regiochemistry in compounds **8-11** was again based on ^{13}C NMR spectroscopy.[21] Typical effects of the ketal linkage containing OH-4 and OH-6 on the ^{13}C chemical shifts were observed, as shown in Table 4, in which data for the glucosyl moiety of sucrose acetals are reported (the fructosyl part is unchanged). In deuterated DMSO, C-4 and C-6 were consistently shifted downfield (+10 and +7 ppm respectively, compared to sucrose), whereas C-3 and C-5 were shifted upfield (-3 and -10 ppm respectively). For the peracetylated compounds, the effect at C-3 disappeared. When an axial methyl group is present in the newly created 6-membered ring (compounds **8-11**), the so-called "γ effect" has an opposite effect on the chemical shifts of C-4 and C-6, decreasing to *ca.* +5 and +2 ppm, respectively, the downfield shift observed previously. In addition, ^{1}H NMR spectroscopy showing unchanged H-4 and H-6ab chemical shifts upon acetylation confirmed the proposed structures.[22]

Table 4. ^{13}C NMR chemical shifts for the glucosyl moiety of sucrose derivatives, in d_6-DMSO for unprotected compounds, and in $CDCl_3$ for the peracetylated ones.

	C-1	C-2	C-3	C-4	C-5	C-6
sucrose	91.8	71.7	72.9	69.9	72.9	60.6
2a	92.2	72.2	69.4	80.7	62.5	67.6
2b	92.2	72.2	69.4	80.7	62.5	68.6
6ab	92.2	72.3	69.5	80.9	62.7	67.7
8ab	92.2	72.3	69.3	75.3	63.2	62.8, 62.9
10	92.2	72.4	69.4	75.4	63.2	63.1
Ac_8-sucrose	90.1	68.4	70.4	68.6	69.8	61.9
3a	90.3	69.9	71.0	78.7	63.4	68.2
3b	90.4	68.8	71.1	78.6	63.5	68.2
7ab	90.4	68.7	70.8	78.6	63.5	67.9
9ab	90.3	68.9	71.2	72.7	64.3	63.3
11	90.3	68.9	71.2	72.7	64.3	63.3



Scheme 5

Sensitivity of the reaction to water and heat

Having in hand substantial amounts of acetals **2ab**, we studied the rate of their hydrolysis in comparison with their hydrogenated analogs **6ab**, prepared by catalytic hydrogenation in acetonitrile and characterized as their peracetyl esters **7ab** (Scheme 5).

Under hydrolysing conditions (wet DMF, cat. PPTS), faster cleavage of the unsaturated ketal linkage of **2ab** occurred, leading to citral and sucrose, and finally glucose and fructose. Hydroxymethylfurfural was formed upon heating or longer acidic treatment. In contrast, the 4,6-acetal bonds of the saturated derivatives **6ab** required additional aqueous acid to achieve the hydrolysis which was accompanied by concomitant sucrose hydrolysis and further degradation. This is consistent with the easier transacetalation of dialkyl acetals of unsaturated aldehydes which are more reactive whether the nucleophilic species is an alcohol or water.

Table 5. Reaction of sucrose (2 eq) with CDMA in DMF with 0.02 eq of PPTS, under classical heating (open or closed system) or microwave irradiation.

t (min)	100 °C classical heating closed (N_2)		100 °C classical heating open		100 °C 15W open	
	2ab	**4**	**2ab**	**4**	**2ab**	**4**
2	83	3	59	13	42	17
5	67	11	34	19	33	21
10	63	18	16	26	30	26
30	19	28	11	24	32	18

In Table 5 are given the yields for the reaction of sucrose with CDMA when the mixture is heated. A good yield (83 %) of sucrose acetals **2ab** could be obtained under nitrogen at 100 °C provided that the reaction was carefully cooled and neutralized. With prolonged reaction times, cleavage to acetal **4** occurred. This was compared to the use of microwave heating, which has been reported to be an efficient method for many reaction types,[23,24] notably the synthesis of long chain acetals of L-galactonolactone supported on clays.[25] In our case, such conditions led to total degradation of both sucrose and the aldehyde dimethyl acetals. Using sucrose supported on silica gel as the only acid, CDMA and very little amount of DMF (slurry), irradiation for 2 minutes at 300 W afforded a 7 % yield of **2ab** (16 % after 5 min at 60 W). In DMF solution no improvement of the reaction could be observed except a slower cleavage to compound **4**, as indicated in Table 5. This observation is consistent with a more homogeneous temperature of the system without hot points, confirming the limitation of typical microwave effects for reactions conducted in highly polar solvents.[26-28]

CONCLUSION

The acetalization of unprotected sucrose at the 4,6-position with citral and α- and β-ionones was achieved in satisfactory yields by transacetalization of the dimethyl acetals of the carbonyl substrates.

EXPERIMENTAL

General methods. Nuclear magnetic resonance spectra were recorded on a Brüker AC 200 spectrometer at 50.32 MHz for carbon and 200 MHz for proton. Chemical shifts are given with reference to DMSO or $CDCl_3$ central peaks (39.5 and 77.0 respectively) for carbon, and downfield internal tetramethylsilane for proton. The acetal functionalized carbon in sucrose acetals is referred to as C-7 in NMR spectral descriptions, with increasing numbers (8 to 13) for chain atoms of citrylidene residues. Reactions were monitored by TLC using aluminium silica gel plates ($60F_{254}$). Flash-chromatography separations were performed using silica gel 60H (40-63μ) under a 1 bar pressure. High performance liquid chromatography analyses were performed using NH_2 bound columns (Nucleosil or Spherisorb) with refraction index detection (RI). Mass spectrometry analysis (FAB) was performed at the "Centre d'Etudes et de Recherches sur les Macromolécules Végétales (CERMAV)" in Grenoble. Elemental analyses were performed by the "Service Central d'Analyse du CNRS", Vernaison. Anhydrous DMF was distilled under reduced pressure over calcium hydride. Dimethyl acetals of α- and β-ionone were prepared by reaction in methanol using PPTS (0.02 eq) in the presence of trimethyl orthoacetate (1.5 eq). Neutralisation (Na_2CO_3) followed by filtration and solvent evaporation provided crude dimethyl acetals which were purified by distillation.

General procedure for the synthesis of sucrose acetals. Preparation of acetals 2ab, from citral dimethyl acetal and their peracetylated derivatives 3ab. To a solution of sucrose (1.57 g, 4.6 mmol) and citral dimethyl acetal (0.45 g, 2.3 mmol) in anhydrous DMF (7 mL) was added pyridinium *p*-toluenesulfonate (12 mg, 0.05 mmol). After 20 h of strirring under nitrogen at room temperature, sodium carbonate was added and the mixture was filtered. Evaporation of the solvent under reduced pressure followed by flash chromatography (CH_2Cl_2-Me_2CO-MeOH-H_2O, 56/20/20/4) provided acetal **2ab** as a syrup (0.81 g, 74 %). When present, glucose acetal **4** was isolated in an early fraction. In the case of compounds **2ab**, semipreparative HPLC separation (Nucleosil NH_2 100 Å, 5 μ, 250 mm x 20 mm, MeCN - water, 95/5) gave small amounts of each isomer. Products were characterized at this stage from their ^{13}C NMR spectrum in deuterated DMSO. The

same procedure was also followed starting from citral. Data for **2a:** ^{13}C NMR (d_6-DMSO) δ 16.9, 17.6, 25.5 (Me), 25.6, 38.6 (C-10,11), 61.8, 61.9 (C-1',6'), 62.5 (C-5), 67.6 (C-6), 69.4 (C-3), 72.2 (C-2), 73.9 (C-4'), 76.6 (C-3'), 80.7 (C-4), 82.4 (C-5'), 92.2 (C-1), 98.3 (C-7), 104.0 (C-2'), 121.6, 123.7 (C-8,12), 131.1, 141.4 (C-9,13). $[\alpha]_D^{20}$ + 58 (*c* 1, MeOH). Data for **2b:** ^{13}C NMR (d_6-DMSO) δ 17.6, 22.9, 25.5 (Me), 26.2, 32.4 (C-10,11), 61.8, 61.9 (C-1',6'), 62.5 (C-5), 68.6 (C-6), 69.4 (C-3), 72.2 (C-2), 73.9 (C-4'), 76.6 (C-3'), 80.7 (C-4), 82.4 (C-5'), 92.2 (C-1), 98.1 (C-7), 104.0 (C-2'), 122.7, 123.8 (C-8,12), 131.3, 141.5 (C-9,13). $[\alpha]_D^{20}$ + 77 (*c* 1, MeOH). **2ab:** MS FAB (NH_3) *m/z* 494 ($M+NH_4^+$), 477 ($M+H^+$), 332, 315, 170, 153. Data for **4:** ^{13}C NMR (d_6-DMSO) δ 16.9, 17.5, 17.6, 22.7, 25.5 (Me), 25.6, 26.1, 32.3, 38.5 (CH_2), 61.9 (C-5α), 65.8 (C-5β), 67.7, 67.9 (C-6), 69.6, 72.9, 75.8, 80.4, 80.5, 81.3 (C-2, 3, 4), 93.1, 97.5, 97.9, 98.2, 98.3 (C-1,7), 121.7, 121.8, 122.7, 123.7, 123.9 (CH=), 131.1, 131.2, 141.2, 141.3, 141.4 (C=). MS FAB (NH_3) *m/z* 332 ($M+NH_4^+$), 315 ($M+H^+$), 297, 255, 221. *Peracetylation.* Sucrose acetals were peracetylated (0.7 M in pyridine - acetic anhydride, 3:1 vol.). After stirring for 24 h at 0 °C, the mixture was poured into saturated aqueous sodium carbonate, and the products were extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over sodium sulfate, concentrated and purified by flash chromatography (AcOEt - hexane, 1:1) to give peracetylated acetals (yields over 85 %). This allowed full characterization (^1H and ^{13}C NMR in $CDCl_3$, elemental analysis, specific rotation for single isomers). Data for **3a:** ^1H NMR ($CDCl_3$) δ 1.51 (s, 3 H, Me), 1.60 (s, 3 H, Me), 1.62 (d, *J* = 0.9 Hz, 3 H, Me), 1.98, 2.01, 2.02, 2.03, 2.04, 2.12 (6 s, 18 H, 6 Ac), 1.85-2.20 (m, 4 H, H-10ab, 11ab), 3.43 (t, *J* = 9.8 Hz, 1 H, H-6a), 3.51 (t, *J* = 9.8 Hz, 1 H, H-6b), 3.93-4.27 (m, 7 H, H-4, 5, 1'a, 1'b, 5', 6'a, 6'b), 4.75 (dd, *J* = 10.0, 3.9 Hz, 1 H, H-2), 4.93-5.06 (m, 1 H, H-12), 5.08 (d, *J* = 5.8 Hz, 1 H, H-7), 5.18 (dd, *J* = 5.8, 0.9 Hz, 1 H, H-8), 5.24-5.43 (m, 3 H, H-3, 3', 4'), 5.58 (d, *J* = 3.9 Hz, 1 H, H-1). ^{13}C NMR ($CDCl_3$) δ 17.2, 17.6 (2 Me), 20.5, 20.6, 20.7 (Ac), 25.6 (Me), 26.0, 39.0 (C-10,11), 63.1, 63.3 (C-1',6'), 63.4 (C-5), 68.2 (C-6), 68.9 (C-2), 71.0 (C-3), 74.6 (C-4'), 75.6 (C-3'), 78.7 (C-4), 78.9 (C-5'), 90.3 (C-1), 99.5 (C-7), 103.8 (C-2'), 120.8, 123.6 (C-8,12), 131.9, 143.4 (C-9,13), 169.7, 169.8, 170.1, 170.2, 170.5 (C=O). $[\alpha]_D^{20}$ + 59 (*c* 0.8, $CHCl_3$). Data for **3b:** ^1H NMR ($CDCl_3$) δ 1.54 (s, 3 H, Me), 1.63 (s, 3 H, Me), 1.67 (d, *J* = 1.2 Hz, 3 H, Me), 1.97, 2.01, 2.02, 2.04, 2.12 (5 s, 18 H, 6 Ac), 1.90-2.16 (m, 4 H, H-10ab, 11ab), 3.43 (t,

J = 9.8 Hz, 1 H, H-6a), 3.49 (t, J = 9.8 Hz, 1 H, H-6b), 3.94-4.28 (m, 7 H, H-4, 5, 1'ab, 5', 6'ab), 4.76 (dd, J = 10.0, 3.9 Hz, 1 H, H-2), 4.98-5.12 (m, 1 H, H-12), 5.08 (d, J = 6.3 Hz, 1 H, H-7), 5.19 (dd, J = 6.3, 1.2 Hz, 1 H, H-8), 5.25-5.44 (m, 3 H, H-3, 3', 4'), 5.58 (d, J = 3.9 Hz, 1 H, H-1). ^{13}C NMR ($CDCl_3$) δ 17.7 (Me), 20.6, 20.7 (Ac), 23.3, 25.6 (2 Me), 26.6, 33.0 (C-10,11), 63.2, 63.4 (C-1',6'), 63.5 (C-5), 68.2 (C-6), 68.8 (C-2), 71.1 (C-3), 74.7 (C-4'), 75.5 (C-3'), 78.6 (C-4), 79.1 (C-5'), 90.4 (C-1), 99.2 (C-7), 103.9 (C-2'), 121.8, 123.7 (C-8,12), 132.1, 148.6 (C-9,13), 169.8, 170.1, 170.3, 170.6 (C=O). $[\alpha]_D^{20}$ + 75 (*c* 1.1, $CHCl_3$). Data for **5:** ^{1}H NMR ($CDCl_3$) δ 1.50-1.75 (m, 9 H, Me), 1.88-2.17 (m, 13 H, Ac, H-10ab, 11ab), 3.36-3.63, 3.79-3.96, 4.02-4.26 (3 m, 4 H, H-4, 5, 6ab), 4.93-5.27 (m, 4.4 H, H-2, 3β, 7, 8, 12), 5.44 (t, J = 9.9 Hz, 0.6 H, H-3α), 5.68 (d, J = 8.1 Hz, 1 H, H-1β), 6.19 (d, J = 3.8 Hz, 0.6 H, H-1α). ^{13}C NMR ($CDCl_3$) δ 17.2, 17.5 (Me), 20.4, 20.5, 20.6, 20.7, 20.7, 20.8 (Ac), 23.2, 25.5 (Me), 25.9, 26.5, 32.9, 39.0 (C-10,11), 64.7 (C-5α), 66.8 (C-5β), 67.8, 68.1 (C-6), 68.7, 69.8, 71.1, 71.7 (C-2, 3), 77.6, 78.3 (C-4), 89.5 (C-1α), 92.0 (C-1β), 99.0, 99.1, 99.3, 99.5 (C-7), 120.3, 120.4, 121.3, 121.4, 123.4, 123.5 (C-8,12), 131.8, 132.1, 143.6, 143.7, 143.8, 143.9 (C-9,13), 168.7, 169.0, 169.4, 169.7, 169.8, 169.9 (C=O). MS FAB (NH_3) *m/z* 458 ($M+NH_4^+$), 441 ($M+H^+$), 381, 347, 264, 263, 247, 223.

3ab: Anal. Calcd for $C_{34}H_{48}O_{17}$: C, 56.04; H, 6.64. Found: C, 55.80; H, 6.84.

Procedure for reactions under microwave irradiation. *Reactions in solution.* To a solution of sucrose (3.2 g, 9.4 mmol) in DMF (15 mL) kept at 60 °C was added the aldehyde or its dimethylacetal (4.7 mmol). Part of this mixture (*ca.* 2 g) was placed in the microwave apparatus (Synthewave S402, Prolabo S.A), and the second half, in a flask placed in an oil bath. Then, a 2 % solution of PPTS in DMF (0.15 mL) was added and the mixture was heated (or irradiated) the appropriate time. Then, triethylamine in DMF was added in order to quench rapidly the reaction and to cool down the medium. Purification was performed following the same procedure as above. *Reaction in slurries.* Supported sucrose was prepared by adding silica gel to a solution of sucrose (4.8 g) in DMF (35 mL) warmed at 60 °C, followed by evaporation of the solvent under reduced pressure. Part of this material (3.9 g of the obtained solid, corresponding to 0.95 g of sucrose, 2.8 mmol), was impregnated with citral dimethylacetal (0.358 g, 1.8 mmol), and DMF (1.8 g) to provide a slurry which was placed in the microwave oven and irradiated for 2 minutes at

300 W, or 5 minutes at 60 W. Using the previous work-up, acetals **2ab** were isolated in 7 and 16 % yield, respectively, whereas only a 3 % yield was obtained when heating the same mixture placed in a flask with an oil bath.

Catalytic hydrogenation of 2ab. Preparation of compounds 6ab. To a solution of acetals **2ab** (238 mg, 0.5 mmol) in acetonitrile (30 mL) was added 10 % Pd/C (20 mg) and the mixture was stirred at room temperature under hydrogen (1 atm). Monitoring of the reaction could be achieved using HPLC (NH_2 column, MeCN-H_2O, 90/10). After 2 days, the mixture was filtered through Celite, and solvent was evaporated. Flash-chromatography (same solvent as above) provided hydrogenated acetals **6ab** as a syrup (192 mg, 80 %). Data for **6ab:** ^{13}C NMR (d_6-DMSO) δ 19.7, 19.8, 22.5, 22.6 (Me), 24.0, 24.1 (CH_2), 27.4, 28.3 (C-9-13), 36.8, 37.0, 38.6, 38.7, 41.1, 41.2 (CH_2), 61.8 (C-1',6'), 62.7 (C-5), 67.7 (C-6), 69.5 (C-3), 72.3 (C-2), 73.9 (C-4'), 76.7 (C-3'), 80.9 (C-4), 82.5 (C-5'), 92.2 (C-1), 100.6, 100.7 (C-7), 104.1 (C-2'). Data for **7ab:** ^1H NMR ($CDCl_3$) δ 0.77, 0.80 (m, 9 H, Me), 0.91-1.65 (m, 10 H), 1.99, 2.01, 2.03, 2.04, 2.12 (5 s, 18 H, 6 Ac), 3.33, 3.34 (2t, J = 9.8 Hz, 1 H, H-6a), 3.42 (t, J = 9.8 Hz, 1 H, H-6b), 3.88-4.27 (m, 7 H, H-4, 5, 1'ab, 5', 6'ab), 4.43-4.53 (m, 1 H, H-7), 4.75 (dd, J = 10.0, 3.9 Hz, 1 H, H-2), 5.24-5.44 (m, 3 H, H-3, 3', 4'), 5.58 (d, J = 3.9 Hz, 1 H, H-1). ^{13}C NMR ($CDCl_3$) δ 19.8 (Me), 20.5, 20.6, 20.7 (Ac), 22.5, 22.6 (Me), 24.5 (CH_2), 27.9, 28.8, 28.9 (CH), 37.2, 37.3, 39.1, 39.9, 41.0 (CH_2), 63.1, 63.2 (C-1',6'), 63.5 (C-5), 67.9 (C-6), 68.7 (C-2), 70.8 (C-3), 74.6 (C-4'), 75.5 (C-3'), 78.6 (C-4), 79.0 (C-5'), 90.4 (C-1), 101.9, 102.0 (C-7), 103.9 (C-2'), 169.8, 170.1, 170.3, 170.5 (C=O).

6ab: Anal. Calcd for $C_{34}H_{52}O_{17}$: C, 55.73; H, 7.15. Found: C, 55.41; H, 7.17.

α-Ionone sucrose acetals and their peracetylated derivatives (8ab, 9ab). See general procedure. Data for **8ab:** ^{13}C NMR (d_6-DMSO) δ 22.3, 22.5 (CH_2), 22.6, 22.7, 26.9, 27.0, 27.2, 29.3, 29.6, 30.7 (Me), 31.4, 31.6 (CH_2), 31.7, 31.8 (C), 53.2, 53.3 (CH), 61.8, (C-1',6'), 62.8, 62.9 (C-6), 63.2 (C-5), 69.3 (C-3), 72.3 (C-2), 73.8 (C-4'), 75.3 (C-4), 76.6 (C-3'), 82.5 (C-5'), 92.2 (C-1), 99.7 (C-7), 104.0 (C-2'), 121.0, 121.1 (CH=), 131.6, 131.9 (CH=), 133.1, 133.2, 134.7, 135.1 (C=). Data for **9ab:** ^1H NMR ($CDCl_3$) δ 0.75 (s, 3 H, Me), 0.81 (s, 3 H, Me), 1.28 (s, 3 H, Me), 1.49 (s, 3 H, Me), 1.95, 1.97, 1.98, 2.00, 2.08 (5 s, 18 H, 6 Ac), 1.90-2.15 (m, 4 H), 3.44-3.67 (m, 2 H, H-6ab), 3.76-4.24 (m, 7 H, H-4, 5, 1'ab, 5', 6'ab), 4.62, 4.64 (2 dd, J = 9.9, 3.9 Hz, 1 H, H-2), 5.16-

5.38 (m, 3 H, H-3, 3', 4'), 5.44 (dd, J = 9.4, 4.6 Hz, 1 H, CH=), 5.53 (d, J = 3.9 Hz, 1 H, H-1). ^{13}C NMR ($CDCl_3$) δ 20.4, 20.5, 20.6, 20.7 (Ac), 22.8, (Me), 28.9 (CH_2), 26.9, 27.4, 29.2 (Me), 31.7 (CH_2), 32.0, 32.1 (C), 53.8, 54.0 (CH), 63.2 (C-1',6'), 63.3 (C-6), 64.3 (C-5), 68.9 (C-2), 71.2 (C-3), 72.7 (C-4), 74.7 (C-4'), 75.5 (C-3), 79.1 (C-5'), 90.3 (C-1), 100.7 (C-7), 103.9 (C-2'), 121.4, 121.5, 130.8 (CH=), 133.0, 133.1 (C=), 136.1, 136.2 (CH=), 169.6, 169.7, 170.0, 170.3, 170.5.

9ab: Anal. Calcd for $C_{37}H_{52}O_{17}$: C, 57.80; H, 6.82. Found: C, 57.94; H, 7.10.

β-Ionone sucrose acetal and its peracetylated derivative (10, 11). See general procedure. Data for **10:** ^{13}C NMR (d_6-DMSO) δ 18.8 (CH_2), 21.2, 28.5, 28.6, 29.3 (Me), 32.1 (CH_2), 33.7 (C), 38.8 (CH_2), 61.9, 62.0 (C-1',6'), 63.1 (C-6), 63.2 (C-5), 69.4 (C-3), 72.4 (C-2), 73.9 (C-4'), 75.4 (C-4), 76.7 (C-3'), 82.5 (C-5'), 92.2 (C-1), 100.0 (C-7), 104.0 (C-2'), 128.4 (C=), 131.3, 133.5 (CH=), 136.2 (C=). $[\alpha]_D^{20}$ + 50 (*c* 1, MeOH). Data for **11:** ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 6 H, Me), 1.39 (s, 3 H, Me), 1.65 (s, 3 H, Me), 1.99, 2.01, 2.03, 2.04, 2.14 (5 s, 18 H, 6 Ac), 1.30-2.10 (m, 6 H), 3.55-3.75 (m, 2 H, H-6ab), 3.84-4.42 (m, 7 H, H-4, 5, 1'ab, 5', 6'ab), 4.68 (dd, J = 10.0, 3.9 Hz, 1 H, H-2), 5.18-5.42 (m, 3 H, H-3, 3', 4'), 5.57 (d, J = 3.9 Hz, 1 H, H-1), 6.13 (brd, J = 16.5 Hz, 1 H, CH=). ^{13}C NMR ($CDCl_3$) δ 19.0 (CH_2), 20.5, 20.6, 20.7 (Ac), 21.5, 28.7 (Me), 29.2 (CH), 32.6 (CH_2), 34.0 (C), 39.2 (CH_2), 63.1, 63.2 (C-1',6'), 63.3 (C-6), 64.3 (C-5), 68.9 (C-2), 71.2 (C-3), 72.7 (C-4), 74.7 (C-4'), 75.5 (C-3), 79.1 (C-5'), 90.3 (C-1), 101.1 (C-7), 103.9 (C-2'), 129.3 (C=), 132.3, 132.6 (CH=), 136.3 (CH=), 169.7, 169.8, 169.8, 170.1, 170.3, 170.5. $[\alpha]_D^{20}$ + 68 (*c* 1, $CHCl_3$).

11: Anal. calcd for $C_{37}H_{52}O_{17}$: C, 57.80; H, 6.82. Found: C, 57.59; H, 6.95.

ACKNOWLEGMENT

Financial support from Béghin-Say and CNRS is gratefully acknowledged. We thank Professor J. Gelas (Clermont-Ferrand) for supportive discussions and for sending us a preprint of his recent article (ref. 9).

REFERENCES AND NOTES

1. Dedicated to Professor Hans Paulsen, on the occasion of his 75th birthday, in recognition for his accomplishments in the field of carbohydrate chemistry.

2. Present address: Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-242 Warszawa, Poland.
3. R. Khan, *Pure Appl. Chem.*, **56**, 883 (1984); C. E. James, L. Hough and R. Khan in *Progress in the Chemistry of Organic Natural Products*, Vol. 55, 118 (1989).
4. S. Jarosz, *Polish J. Chem*, **70**, 972 (1996).
5. S. Houdier and S. Perez, *J. Carbohydr. Chem.*, **14**, 1117 (1995).
6. S. B. Engelsen, C. Hervé du Penhoat and S. Perez, *J. Phys. Chem.*, **99**, 13334 (1995).
7. S. Immel and F. W. Lichtenthaler, *Liebigs Ann. Chem.*, 1925 (1995).
8. E. Fanton, C. Fayet, J. Gelas, D. Jhurry, A. Deffieux and M. Fontanille, *Carbohydr. Res.*, **226**, 337 (1992).
9. E. Fanton, C. Fayet and J. Gelas, *Carbohydr. Res.*, **298**, 85 (1997).
10. E. Fanton, J. Gelas, D. Horton, H. Karl, R. Khan, C.-K. Lee and G. Patel, *J. Org. Chem.*, **46**, 4057 (1981).
11. G. O. Aspinall, I. H. Ibrahim and N. K. Khare, *Carbohydr. Res.*, **200**, 247 (1990).
12. P. A. Wallace and D. E. Minnikin, *Carbohydr. Res.*, **263**, 43 (1994).
13. R. Nouguier, V. Mignon and J.-L. Gras, *Carbohydr. Res.*, **277**, 339 (1995).
14. M. E. Evans, *Carbohydr. Res.*, **21**, 473 (1972).
15. J. Gelas, *Adv. Carbohydr. Chem. Biochem.*, **39**, 71 (1981).
16. D. M. Clode, *Chem. Rev.*, **79**, 491 (1979).
17. F. H. Bissett, M. E. Evans and F. W. Parrish, *Carbohydr. Res.*, **5**, 184 (1967).
18. J. Kula, B. Bragiel and J. Gora, *Parf. Kosmetik*, **76**, 368 (1995).
19. For a review on acetalization reactions, see: F. A. J. Meskens, *Synthesis*, 501 (1981).
20. T. Tsunoda, M. Suzuki and R. Noyori, *Tetrahedron Lett.*, **21**, 1357 (1980).
21. For a review on carbon nuclear resonance spectroscopy of monosaccharides, see: K. Bock and C. Pedersen, *Adv. Carbohydr. Chem. Biochem.*, **41**, 27 (1983).
22. A. De Bruyn, M. Anteunis and G. Verhegge, *Carbohydr. Res.*, **42**, 157 (1975).
23. A. Loupy and A. Audrechy, *Effets de Milieu en Synthèse Organique*, Masson, Paris, 1996.
24. S. Caddick, *Tetrahedron*, **51**, 10403 (1995).
25. M. Csiba, J. Cleophax, A. Loupy, J. Malthête and S. D. Gero, *Tetrahedron Lett.*, **34**, 1787 (1993).
26. S. D. Pollington, G. Bond, R. B. Moyes, D. A. Whan, J. P. Candlin and J. R. Jennings, *J. Org. Chem.*, **56**, 1313 (1991).
27. R. Laurent, A. Laporterie, J. Dubac, J. Berlan, S. Lefeuvre and M. Audhuy, *J. Org. Chem.*, **57**, 7099 (1992).
28. K. D. Raner, C. R. Strauss, F. Vyskoc and L. Mokbel, *J. Org. Chem.*, **58**, 950 (1993).