Assignment of Absolute Configuration of α-threo Benzylidene Acetals of Acylic Derivatives of Arabinose Using N.m.r. Spectroscopy

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Summay: The principal 2,3:4,5-diacetyal obtained by benzylidenation of L-arabinose dietyl dithioacetal with benzaldehyde/hydrogen chloride has been assigned the R configuration at the 2,3-acetal centre following its conversion into 2,3-O-(R)-benzylidene-L-arabinitol. The configuration of the latter compound was established by its conversion into "trans" 1,4-di-O-benzoyl-2, 3-O-benzylidene-erythritol by sequential periodate oxidation, epimerisation of the resulting 2,3-O-(R)-benzylidene-L-threose to give 2,3-O-(R)-benzylidene-L-erythrose, reduction, and benzoylation.

Introduction

As a part of study of the benzylidene acetals of arabinose, arabinitol, and their derivatives, it was necessary to assign the configuration at the 2,3-acetal centre of 2,3:4,5-di-O-benzylidene-L-arabinose diethyl dithioacetal (1). The 2,3-acetal comprises a substituted 1,3-dioxolane ring, and it has been shown by ^{1}H-n.m.r spectroscopy that a number of benzylidene acetals containing 1,3-dioxolane rings are mixtures of diastereoisomers [1,2]. Configuration can be assigned to pairs of diastereoisomeric substituted, 1,3-dioxolane derivatives on the basis of the observed differences in chemical shifts of the acetal hydrogen atoms, dependent on the nature of the cis-substitutents at positions 4 and 5 [1-3]. However, this method is not applicable to 2,3-acetals in the acylic arabino series and to other α-threo acetals because, for each diastereoisomer, one hydrogen and one carbon substituent are in cis relationship to the acetal hydrogen. We now report on the conversion of the diacetal (1) into a compound in which there are characteristic differences in chemical shift for the acetal hydrogens of the two isomers which permit assignments of configuration.

Discussion

Treatment of L-arabinose diethyl dithioacetal with benzaldehyde and hydrogen chloride gave crystalline 2,3:4,5-di-O-benzylidene-L-arabinose diethyl dithioacetal (1) as the principal product (~ 40% yield). Compound (1) has previously been described by Huebner et al. [4] and Zinner et al. [5] (D enantiomer). The N.m.r. spectrum ($CDCl_3$) of the diacetal (1) showed two benzyl proton signals(δ 6.15 and 5.8) in agreement with the diacetal structure and suggesting that (1) was probably a single diastereoisomer. Partial hydrolysis of (1) with acetic acid, following the procedure described by Huebner et al. [4], gave

crystalline 2,3-O-benzylidene-L-arabinose diethyl dithioacetal (2), which gave a single benzyl proton signal(δ 6.1) in its N.m.r. spectrum ($CDCl_3$). This evidence suggested that (2) was probably a single benzylidene isomer, and confirmation of this conclusion was sought by conversion of (2) into 2,3-O-benzylidene-L-arabinitol. Thus, demercaptalation of the dithioacetal (2) with mercuric chloride/mercuric oxide followed by reduction of the resulting aldehyde with sodium borohyride gave 2,3-O-(R)-benzylidene-L-arabitol (3), m.p. 104-105°. This compound was indistinguishable from an authentic isomer of 2,3,-O-benzylidene-L-arabinitol prepared [6] by benzylidenation of 1,5-di-O-benzoyl-L-arabinitol followed by chromatographic fractionation of the diastereoisomeric mixture of 2,3-acetals and debenzoylation [the diastereoisomer of 3 had [6] m.p. 81-82°].

As already stated, it was not possible to assign the configuration of the α-threo2,3-acetal group in 3 by using n.m.r chemical shift of the benzyl proton because, in both isomers, this proton is cis to an alkyl substituent on the 1,3-dioxolane ring. This situation results in very similar chemical shifts for the benzyl protons in the two isomers. It was therefore necessary to convert the 2,3-acetal (3) into a compound for which there would be a grater difference in chemical shift for the acetal hydrogen of the two isomers. For this purpose, (3) was converted into 2,3-O-(R)-benzylidene-L-threose (4) by oxidation with sodium periodate, and the syrupy 4 was then isomerised with methanolic sodium methoxide to yield crystalline 2,3-O-(R)-benzylidene-L-erythrose (5). Acid hydrolysis of 5 gave a single compound having the same paper-chromatographic mobility as authentic D-erythrose. Compound 5 was not previously known although a 2,3-O-benzylidene-D-erythrose has been obtained as a syrup [7], and direct comparison of physical constants was therefore not possible.

For the assignment of configuration at the acetal centre, compound 5 was reduced with sodium borohydride to give crystalline "trans"-2,3-O-benzylidene-erythritol (6), which was characterised as the crystalline dibenzoate (7). These compounds,which were previously unknown, both gave single benzyl proton signals in their n.m.r. spectra. Compound 7 was then compared with the authentic "cis and "trans" isomers of 1,4-di-O-benzoyl-2,3,-O-benzylidene-erythritol prepared as follows. Benzylidenation of 1,4-di-O-benzoylerythritol with benzaldehyde and zinc chloride gave the known [7] crystalline "cis, trans"-1,4-di-O-benzoyl-2,3-O-benzylidene-erythritol, which gave two benzyl proton signals in its n.m.r. spectrum at δ 6.35 and 5.95 in the ratio 1:3. The high-field signal at δ 5.95 is assigned to the "cis" isomer 8 and the low-field signal at 6.35 is assigned to the "trans" isomer 7. Compound 8, arbitrarily defined as the "cis" isomer, has the acetal proton on the same side of the 1,3-dioxolane ring as the hydrogen atoms at C-4 and C-5, whereas the "trans" isomer (7) has the acetal proton on the opposite side. The "cis,trans" mixture was then fractionated by chromatography on silica gel to yield the individual crystalline diastereoisomers (7) and (8). "Trans"-1,4-Di-O-benzoyl-2,3-O-benzylidene-erythritol 7, m.p. 99-101°, benzyl proton signal at δ 6.35, was indistinguishable from the benzoylated product of the reduction of (5) [obtained by the sequence 3 → 4 → 5 → 6 → 7].

The base-catalysed epimerisation of aldoses at C-2 is a well known route

for the interconversion of sugar [8]. The mechanism has been thoroughly explored and its is expected that the configuration at C-3 and at the acetal centre should be unaffected by the epimerisation at C-2 of 4 and also by the previous periodate oxidation. Therefore, the isolation of "trans" -2, 3-O-benzylidene-etythritol (6) shows that 3, 4, and 5 all have the R configuration at the 2,3-acetal centre.

The foregoing identification of compound 3 as 2,3-O-(R)-benzylidene-L-arabinitol enables the R configuration to be assigned to the 2,3-acetal centre in the dithioacetals 1 and 2, provided that isomerisation does not occur during the partial hydrolysis and demercaptalation/reduction reactions involved in the conversions 1 → 2 → 3. Each of these reactions gave a single diastereoisomer and, since isomerisation would not be expected to lead to only a single product, it is concluded that the acetal configurations in the dithioacetals 1 and 2 are the same as that in 3. Although the yield of 3 was low (~ 12%) probably because of solubility problems during the recovery of 3, application of the demercaptalation/reduction procedure to the 4,5-O-isopropylidene derivative of 2 gave a 63% yield of 2,3-O-(R)-benzylidene-4,5-O-isopropylidene-L-arabinitol. This compound was identical with the product obtained acetonation (acetone /$CuSO_4$) of 2,3-O-(R)-benzylidene-L-arabinitol (3), and partial acid hydrolysis, of 2,3-O-(R)-benzylidene -4,5-O-isopropylidene-L-arabinitol gave only 3. The retention of the R configuration at the 2,3-acetal centre during these transformations supports the conclusion that isomerisation did not occur during the sequence 1 → 2 → 3.

The assignment of the R configuration to the 2,3-acetal centre in 2,3:4, 5-di-O-benzylidene-L-arabinose diethyl dithioacetal (1) supports the conclusion that 1 is probably a single diastereoisomer, but the configuration at the 4,5-acetal centre remains to be established.

Experimental

General methods

N.m.r spectra were recorded for 5% solutions in $CDCl_3$ (internal Me_4Si) unless stated otherwise, with a Perkin -Elmer R10 (60 MHz) spectrometer. Pyridine was dried by distillation five times from phosophorus pentaoxide and stored over sodium hydroxide pellets.

Benzylidenation of L-arabinose diethyl dithioacetal

Dry hydrogen chloride was bubbled at 0° through a suspension of L-arabinose diethyl dithioacetal (20 g) in freshly distilled benzaldehyde (50 ml) until a clear solution was obtained (~ 5 min). This solution was stored at 0° until crystallisation started, and ice-cold ethanol (120 ml) was then added. After 30 min, the resulting solid was filtered-off and washed with ice-cold ethanol until the filtrate was neutral (pH 7). Recrystallisation from ethanol gave 2,3:4,5-di-O-benzylidene-L-arabinose diethyl dithioacetal (1) as silky needles (13 g, 40%), m.p. 99-100°, $[\alpha]_D^{27}$ - 12.1° (c 3, chloroform). The N.m.r. spectrum ($CDCl_3$) for 1 showed singlets at 6.15 and 5.8 for the benzyl protons. Huebner et al. [4] reported m.p. 103-105°, $[\alpha]_D^{25}$ - 12.2° (c 5.0, chloroform), for this compound. Zinner et al. [5] reported m.p. 103-105°, $[\alpha]_D^{20}$ + 12.6° (c 2.2,chloroform),for the D enantiomer.

Anal. Calc. for $C_{23}H_{28}O_4S_2$: C, 63.9; H, 6.4; S, 14.9. Found: C, 63.8; H, 6.8; S, 15.1.

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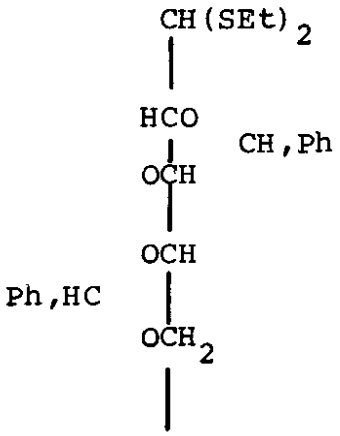
Anal. Calc. for $C_{23}H_{28}O_4S_2$: C, 63.9; H, 6.4; S, 14.9. Found: C, 63.8; H, 6.8; S, 15.1.



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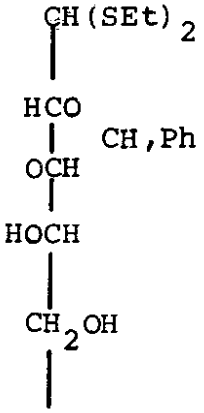

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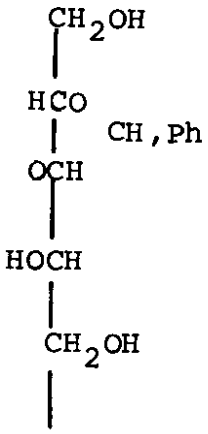

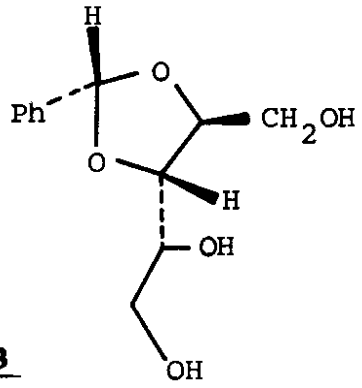

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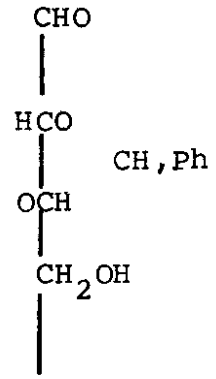

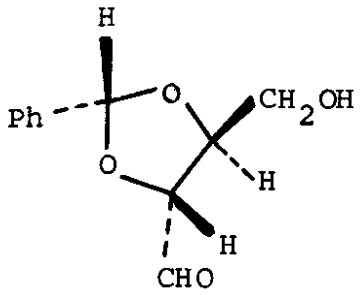

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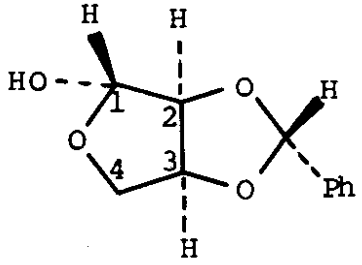

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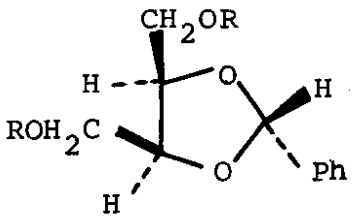
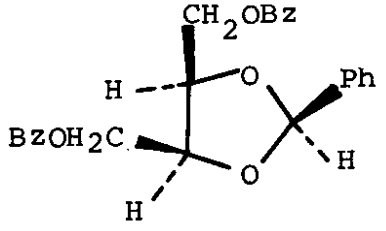


6 R=H

7 R=Bz



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2,3-O-(R)-benzylidene-L-arabinitol (3)

Using the method of Huebner et al. [4], the diacetal 1 was converted by partial hydrolysis with acetic acid into 2,3-O-benzylidene-L-arabinose diethyl dithioacetal (2), m.p. 95-96°, $[\alpha]_D^{23}$ - 16° (c 1.8, chloroform); Huebner et al. [4] recorded m.p. 102-103°, $[\alpha]_D^{25}$ - 25° (c 1.8, chloroform), for this compound.

Compound 2 (0.5 g) was dissolved in acetone (8 ml), and water (4 drops) was added. After the addition of yellow mercuric oxide (0.8 g), the mixture was stirred at 30° for 30 minutes. A solution of mercuric chloride (600 mg) in acetone (6 ml) was then added dropwise with vigorous stirring, and the mixture was heated at 30° for 1 h, at 40° for 1 h, at 50° for 1 h, and under reflux for 1.5 h. Aqueous sodium carbonate (4%) was then added until precipitation was complete, the mixture was filtered, and the residue was washed with acetone (25 ml). Concentration of the combined filtrate and washings under diminshed pressure gave a syrup (0.4 g) which showed one component (R_f 0.6) in t.l.c. (Kieselgel G, Merck; chloroform -ethanol, 9:1).

The foregoing syrup (400 mg) was dissolved in ethanol (40 ml) and water (10 ml), and sodium borohydride (200 mg) was added. The mixture was stored at room temperature overnight with constant strring and then concentrated under diminished pressure. Water (25 ml) was added and the solution was extracted continuously for 24 h with chloroform containing a little ammonia. The dried ($MgSO_4$) extract was concentrated under diminished pressure, and crystallisation of the residue from chloroform gave compound 3 (40 mg, 12%), m.p. 104-105°, $[\alpha]_D^{32}$ - 14.9° (c 2, pyridine). The N.m.r. spectrum ($HCONMe_2$) of 3 showed a single benzyl proton singlet at 5.9.

Anal. Calc. for $C_{12}H_{16}O_5$: C, 60.0; H, 5.7. Found: C, 59.9; H, 6.7.

The mixture m.p. of 3 with a sample of 2,3-O-benzylidene-L-arabinitol (single isomer, m.p. 104-105°, prepared [6] from 1,5-di-O-benzoyl-L-arabinitol) was 104-105°, and the i.r. spectra of the two compounds were eindistinguishable. The diastereoisomeric 2,3-acetal had [6] m.p. 81-82°.

2,3-O-(R)-Benzylidene-L-erythrose (5)

A solution of sodium metaperiodate (800 mg) in water (14 ml) was added to a solution of 2,3-O-(R)-benzylidene-L-arabinitol (3) (400 mg) in phosphate buffer (pH 7, 40 ml). After 18 h, the solution was saturated with sodium chloride and extracted with ether (5 x 50 ml). The dried (K_2CO_3) extract was concentrated under diminished pressure to give syrupy 2,3-O-(R)-benzylidene-L-threose (4) (400 mg), $[\alpha]_D^{24}$ - 15.3° (c 2.6, ethanol).

Compound 4 (400 mg) was dissolved in methanolic sodium methoxide (440 mg of sodium dissolved in 100 ml of dry methanol). The mixture was stored overnight at room temperature with constant stirring, then neutralised with CO_2 gas, and concentrated under diminished pressure. The residue was dissolved in water (50 ml) and extracted with chloroform (3 x 50 ml). The dried ($MgSO_4$) extract was concentrated to give a syrup (320 mg) that

was purified by chromatography on a column of silica gel (40 g) with chloroform-ethanol (99:1), to give 5 (200 mg, 50%), m.p. 87-89°, (from chloroform-hexane), $[\alpha]_D^{24}$ + 66° (c 1, ethanol). The n.m.r. spectrum ($CDCl_3$) of 5 showed a single benzyl proton singlet at 6.0.

Anal. Calc. for $C_{11}H_{12}O_4$: C, 63.5; H, 5.8. Found: C, 63.2: H, 5.7.

A solution of 5 (10 mg) in aqueous 10% acetic acid (5 ml) was boiled under reflux for 1 h. The solution was then evaporated to dryness and the syrupy residue was washed with ether (2 x 5 ml). Paper chromatography (butanone saturated with water) showed one component which had the same mobility as an authentic samples of D-erythrose.

"trans"-2,3-O-Benzylidene-erythritol (6)

2,3-O-(R)-Benzylidene-L-erythrose (5) (50 mg) was dissolved in aqueous 60% ethanol (5 ml), and sodium borohydride (50 mg) was added. The mixture was stored overnight at room temperature and then evaporated under diminished pressure. Water (10 ml) was added to the residue, and the resulting solution was extracted with chloroform (3 x 15 ml). The combined and dried ($MgSO_4$) extract was concentrated to give a syrup (60 mg) that crystallised from chlorofom-hexane to give 6, m.p. 103°. The n.m.r. spectrum (1,4-dioxane) showed a benzyl proton singlet at 6.1.

Anal. Calc. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.7. Found: C, 62.7; H. 6.5.

"trans"-1,4-Di-O-benzoyl-2,3-O-benzylidene-erythritol (7)

Compound 6 (55 mg) was dissolved in dry pyrdine (5 ml), benzoyl chloride (0.2 ml) was added at 0°, and the mixture was stored overnight at room temperature. Most of the pyridine was then evaporated under diminshed pressure, the residue was poured into ice-water, and the resulting solid was recrystallised from chloroform-hexane to give 7 (60 mg, 54%), m.p.100-101°. The n.m.r. spectrum ($CDCl_3$) showed a benzyl proton singlet at 6.35.

Anal.Calc. for $C_{25}H_{22}O_6$: C, 71.8; H, 5.3. Found: C, 71.8; H, 5.6.

"cis,trans"-1,4,-Di-O-benzoyl-2,3-O-benzylidene-erythritol

A mixture of 1,4-di-O-benzoylerythritol [9] (2 g), commercial fused zinc chloride (2 g), and freshly distilled benzaldehyde (10 ml) was shaken overnight at room temperature and then poured into a vigorously stirred mixture of ice-water and light petroleum (b.p. 60-80°). The resulting crystalline precipitate was recrystallised from chloroform-hexane. The first crop of crystals consisted of the starting dibenzoate (120 mg), but concentration of the mother liquor and recrystallisation of the residue from the same solvent afforded the title compound (1.5 g), m.p. 86-89°. T.l.c. (Kieselgel G, Merck; hexane-ether, 3:2) revealed two components with R_f 0.5 (major) and 0.64 (minor). The n.m.r. spectrum ($CDCl_3$) of the mixture showed two benzyl proton singlets at 6.35 and 5.95 in the ratio 1:3.

Fractionation of the mixture on a column of silica gel (Merck 7734, 50 g) with hexane-ether (2:1) gave, first, "trans"-1,4-di-O-benzoyl-2,3-O-benzylidene-erythritol 7 (90 mg), m.p. 99-101° (from chloroform-hexane), which was indistinguishable (mixture m.p., n.m.r. spectrum, i.r. spectrum) from the samples of 7 prepared from 5 and 6.

Continued elution then gave "cis"-1,4-di-O-benzoyl-2,3-O-benzylidene-erythritol (8) (250 mg), m.p. 85-87° (from chloroform-hexane), benzyl proton singlet at 5.95.

Anal. Calc. for $C_{25}H_{22}O_6$: C, 71.8; H, 5.3. Found: C, 71.8; H, 5.5.

2,3-O-(R)-Benzylidene-4,5-O-isopropylidene-L-arabinose diethyl dithioacetal

Compound 2 (0.6 g) was dissolved in dry acetone (90 ml), anhydrous copper sulphate (2.4 g) was added, and the mixture was stored at room temeprature for 48 h with constant stirring and then filtered. The residue was washed with acetone (50 ml), and the filtrate and washings were combined and evaporated. The resulting syrup (0.8 g) was purified by chromatography on a column of silica gel (Merck 7734, 50g) with chloroform to give the title compound (0.5 g, 75%), m.p. 54° (from hexane), $[\alpha]_D^{21}$ - 32° (c 1, chloroform). The n.m.r. spectrum ($CDCl_3$) showed a benzyl proton singlet at 6.0.

Anal. Calc. for $C_{19}H_{28}O_4S_2$: C, 59.4; H, 7.3 Found C, 59.2; H, 7.1.

2,3-O-(R)-Benzylidene-4,5-O-isopropylidene-L-arabinitol

(a) 2,3-O-(R)-Benzylidene-L-arabinitol (3) (100 mg) was dissolved in dry (K_2CO_3) acetone (15 ml), anhydrous copper sulphate (400 mg) was added, and the mixture was stored at room temperature for 3 days with constant stirring. The mixture was then processed as described in the preceding experiment, to give the title compound (60 mg, 51%), m.p. 57° (from hexane) $[\alpha]_D^{25}$ - 6.6° (c, 0.9, chloroform).

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.3; H, 7.2. Found: C, 64.3; H, 7.4.

(b) A solution of 2,3-O-(R)-benzylidene-4,5-O-iosopropylidene-L-arabinose diethyl dithioacetal (400 mg) in acetone (6 ml) and water (1 ml) was treated with yellow mercuric oxide (600 mg) and mercuric chloride (500 mg) as described in the demercaptalation of compound 2. The resulting syrupy aldehyde (280 mg) was then reduced with sodium borohydride (100 mg) with processing of the reaction mixture as decribed in the preparation of (3), to give the title compound (210 mg 63%), m.p. 57° (from hexane), $[\alpha]_D^{24}$ - 7° (c 1, chloroform), identical (mixture m.p., i.r. spectrum) with the product obtained in (a).

The title compound (100 mg) was dissolved in a solution (3 ml) of toluene-p-sulphonic acid in aqueous 1,4-dioxane (50 mg of toluene-p-sulphonic acid in 4,5 ml of 1,4-dioxane and 0.5 ml of water). The solution was stored overnight at room temperature, then neutralised with aqueous sodium hydrogen corbonate, and continuously extracted for 18h with chloroform containing a little ammonia. The dried ($MgSO_4$) extract was evaporated and crystallisation of the residue from chloroform gave 2,3-O-(R)-benzylidene-L-arabinitol (3) (40 mg, 47%), m.p. 104-105°, identical (mixture m.p., i.r. spectrum) with the authentic compound 3.

References

1. N.Baggett, K.W. Buck, A.B. Foster, M.H. Randall, and J.M. Webber,

J.Chem.Soc., 3394 (1965).
2. D.M. Clode, *Chem.Rev., 79, 491 (1979).*
3. N. Baggett, J.M. Duxbury, A.B. Foster, and J.M. Webber, *J.Chem.Soc., C, 208 (1966).*
4. C.F. Huebner, R.A. Pankrtaz, and K.P. Link, *J.Am.Chem.Soc., 72, 4811 (1950).*
5. H. Zinner, H. Voigt, and J. Voigt, *Carbohydr.Res., 7, 38 (1968).*
6. N. Baggett, N.I. Toufeek, and J.M. Webber, *Unpublished results.*
7. N. Baggett, K.W. Buck, A.B. Foster, B.H. Rees, and J.M. Webber, *J.Chem.Soc., C, 212 (1966).*
8. J.C. Speck, Jr., *Adv.Carbohydr.Chem., 13, 63 (1958).*
9. H. Ohle and G.A. Melkonian, *Ber., 74, 291 (1941).*