REDUCTION OF SULFONYL ESTERS OF ALDOSES WITH SODIUM HYDROGEN BIS(2-METHOXYETHOXY)ALUMINATE*

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A series of primary and secondary sugar *p*-toluenesulfonyl and methanesulfonyl esters was prepared, which were reduced with sodium hydrogen bis(2-methoxyethoxy)aluminate. The reductions took place more rapidly than analogous reductions with lithium aluminum hydride. From secondary *p*-toluenesulfonyl esters corresponding hydroxy compounds were formed, while the primary esters gave a mixture of hydroxy and deoxy derivatives by cleavage of the S—O or the C—O bond, respectively. The ratio of the cleavage of S—O to C—O bonds was higher than in the case of lithium aluminum hydride reduction, and the relative reaction rates of the individual *p*-toluenesulfonyloxy groups also differed.

Some years ago the preparation of sodium hydrogen bis(2-methoxyethoxy)-aluminate, $NaH_2Al(OCH_2CH_2OCH_3)_2$, was described, as well as its use as a reducing agent[1]. Its reactivity[2–10] and physical properties[11] are summarized in a review article[12]. This hydride closely resembles lithium aluminum hydride in its properties, but it is well soluble even in non-polar solvents (benzene, xylene *etc.*).

We now tried to use this reagent (a 70% solution in benzene, "Synhydride") in the chemistry of sugars, either as a substitute for lithium aluminum hydride, if the expected products are the same, or as a selective reducing reagent, if the expected reduction products or the ratio of the isomers formed are different. Since in some of our latest studies[13–16] we investigated the reduction of *p*-toluenesulfonyl esters with lithium aluminum hydride, and in view of the fact that these esters are often used in sugar chemistry, we have investigated in this paper the reduction of some *p*-toluenesulfonyl esters and methanesulfonyl esters with sodium hydrogen bis(2-methoxyethoxy)aluminate.

The substances with a primary *p*-toluenesulfonyloxy group of varying steric accessibility were reduced, such as derivatives of hexofuranoses (*Ia*, *Ib*) and hexopyranoses (*IIa*, *IIb*, *IIIa*, *IVa*, *Va*, *Vb*), further compounds with a secondary *p*-toluenesulfonyl or methanesulfonyl group in the position 2 (*Va*), 3 (*VIa*, *VIIa*), 4 (*IIa*)

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and 5 (*VIIIa*). All these substances were prepared by methods common in sugar chemistry.

Reductions with Synhydride were in all instances carried out with excess reagent. In the case of substances soluble in benzene, benzene solutions of both components were mixed and the mixture was heated to boiling point, if necessary. In the majority of cases the same results were achieved irrespective of whether the substance solution was added to excess hydride solution, or vice versa. However, the first procedure was generally better, because of the permanent presence of the reducing agent during the reaction; under such conditions the side-reactions, caused by the alkaline medium (formation of anhydro derivatives, hydrolysis, *etc.*), were suppressed to a minimum and the results were well reproducible. The substances which were poorly soluble in benzene were added to the reaction mixture in suspension, or else some other solvent was chosen, for example tetrahydrofuran. The reaction course was followed by thin-layer chromatography and the reaction time ranged from several minutes to several hours; in general it was shorter than in the case of reductions with lithium aluminum hydride[13,16–19].

According to the nature of the products formed the reaction mixture was decomposed and worked up in various manners. For substances poorly soluble in water the decomposition with sodium potassium tartrate (method *A*) was convenient, for substances of medium solubility decomposition with water and alkali hydroxide solution (method *B*) was suitable, or also with ethanol and water (method *C*), or ethanol alone (method *D*). In contrast to the reduction with lithium aluminum hydride the reaction mixture after reduction with Synhydride and decomposition always contained 2-methoxyethanol which solubilized (and that even in the organic solvent) a certain amount of inorganic salts (least in the case of decomposition with the tartrate and working up by method *A*). After the evaporation of the solvent and the residues of 2-methoxyethanol *in vacuo* the remaining salts were separated by extraction of the residue with organic solvent. Except for the experiments carried out on a microscale we found it convenient not to omit this operation even when the reduction products were later chromatographed. It is true that the residues of the inorganic salts separated well on the column, but they caused poor penetrability of the column. Substances readily soluble in water could be obtained after the decomposition of the reaction mixture with water by filtering the aqueous solutions through ion exchangers (procedure *E*) or in the form of peracetyl derivatives (procedure *F*).

The reduction of individual *p*-toluenesulfonyl esters afforded the following results: Primary tosyloxy groups in furanoses *Ia* and *Ib* were split off in high yield under formation of the corresponding 6-deoxy derivative *Ic* and *Id*, respectively. In the case of sterically less accessible primary tosyloxy groups in 6-tosylpyranosides the steric arrangement of the whole molecule was important for the reaction course. Thus, in compounds with *gluco*-configuration, either containing free hydroxyl groups (*IIIa*), or blocked hydroxyls (*IIa*, *IIb*), 6-deoxy derivative (*IIIb*, *IIc*, *IId*) was obtained in all instances along with a small amount of the corresponding 6-hydroxy compound *IIIc*, *IIe*, *IIf*, even though the yields were somewhat lower than in the case of the reduction of furanoses *Ia*, *Ib*. In the case of derivatives with

galacto-configuration (*IVa*, *Va*, *Vb*), however, no derivative of 6-deoxygalactose was found among the reaction products; the reduction of these compounds afforded products formed by the cleavage of the S—O bond exclusively, under preservation of the hydroxy group in the position 6, *i.e.* compounds *IVb* and *Vc*. The reluctance of the substituents in the position 6 of *galactose*-derivatives toward the reactions of the S_N2 type is known[20]; the reactivity of the substituents in the position 6 is in the case of *galacto*-configuration about 50 times lower than in the case

TABLE I

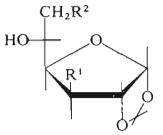
Review of Reductions with Synhydride

Synhydride is a 70% solution of $NaH_2Al(OCH_2CH_2OCH_3)_2$ in benzene.

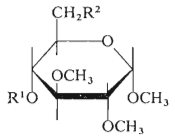
Reduced substance	mg	Reaction time h	Reaction temperature °C	Method of isolation	Product obtained	Yield %	M.p. °C	$[\alpha]_D^{20}$
Ia	1 160	0·5	20	*D*	*Ic*	83·0	37—40	−26·8°
Ib	5 000	0·5	20	*B*	*Id*	81·4	90—92	—
Ib	775	0·5	20	*C*	*Id*	76·0	90—92	—
IIa	1 950	1	80	*B*	*IIc*[a]	62·5	—	+136·8°
					IIe	17·8	80—82	—
IIb	450	1	80	*A*	*IId*[b]	20·5	—	+148·0°
					IIf	67·0	—	+155·1°[c]
IIIa	1 000	1·5	20	*E*	*IIIb*[d]	50·0	—	—
					IIIc[d]	19·5	—	—
					IX[d,e]	2·0	—	—
IIIa	1 000	12	20	*F*[f]	*IIIb*[d]	61·0	—	—
					IIIc[d]	28·0	—	—
IVa	1 300	0·5	80	*B*	*IVb*[g]	95·5	—	—
IVa	1 300	0·5	65	*B*[f]	*IVb*[g]	97·5	—	—
Va	1 000	1	80	*A*	*Va*	4·8	149—150	—
					Vb	67·4	128—129	—
					Vc	23·1	102—103	—
Vb	1 300	2	80	*B*[h]	*Vc*	82·7	102—104	—
Vb	1 300	2	80	*C*[h]	*Vc*	74·0	102—104	—
VIa	200	1	80	*C*	*VIb*	78·0	74—75	—
VIIa	653	1	80	*C*	*VIIb*	75·0	129—131	—
VIIIa	500	12	20	*B*	*VIIIb*	87·0	38—40	−26·5°C

[a] For $C_9H_{18}O_5$ (206·2) calculated: 52·41% C, 8·79% H; found: 52·46% C, 8·92% H; [b] identical with the substance prepared by methylation of methyl 6-deoxy-2,3-di-O-methyl-α-D-glucopyranoside; [c] specific rotation in methanol; [d] isolated in the form of peracetyl derivatives which are characterized in the experimental part; [e] *IX* — methyl 3,6-anhydro-α-D-glucopyranoside; [f] the reduction was carried out in tetrahydrofuran; [g] with *p*-toluenesulfonyl chloride in pyridine it afforded *IVa* quantitatively, m.p. 101—102°C; [h] the reduction was carried out in suspension.

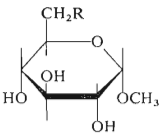
of *gluco*-configuration[21]. This is also observed in the reductions with lithium aluminum hydride[22]. In spite of this conditions have been found[17,22,24] under which, for example, the reduction of 1,2 : 3,4-di-O-isopropylidene-6-O-*p*-toluene-sulfonyl-α-D-galactose[17] (*IVa*) with lithium aluminum hydride afforded 6-deoxygalactose *IVc* in good yield. Analogous reduction of *IVa* with Synhydride led even under these conditions to 6-hydroxy compound *IVb* only.



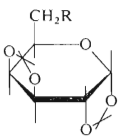
Ia; R^1 = H, R^2 = OTs
Ib; R^1 = OH, R^2 = OTs
Ic; R^1 = H, R^2 = H
Id; R^1 = OH, R^2 = H



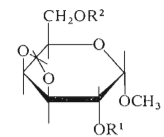
IIa; R^1 = Ts, R^2 = OTs
IIb; R^1 = CH_3, R^2 = OTs
IIc; R^1 = H, R^2 = H
IId; R^1 = CH_3, R^2 = H
IIe; R^1 = H, R^2 = OH
IIf; R^1 = CH_3, R^2 = OH
IIg; R^1 = H, R^2 = OTs



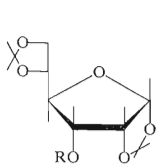
IIIa; R = OTs
IIIb; R = H
IIIc; R = OH



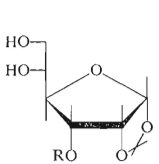
IVa; R = OTs
IVb; R = OH
IVc; R = H



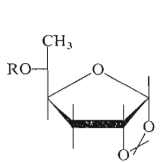
Va; R^1 = Ts, R^2 = Ts
Vb; R^1 = H, R^2 = Ts
Vc; R^1 = Ts, R^2 = H



VIa; R = Ms
VIb; R = H



VIIa; R = Ms
VIIb; R = H



VIIIa; R = Ts
VIIIb; R = H

Secondary *p*-toluenesulfonyl or methanesulfonyl groups in positions 2, 3, 4 and 5 of compounds *Va*, *VIa*, *VIIa*, *IIa*, and *VIIIa* when submitted to the effect of Synhydride split off unambiguously under formation of corresponding hydroxy compounds *Vc*, *VIb*, *VIIb*, *IIc* (together with *IIe*) and *VIIIb*. In view of the fact that *Va*, *VIa*, *IIa* and *VIIIa* are compounds in which an intramolecular reaction[15] cannot be assumed, this result is not surprising. The cleavage of the C—O bond in secondary *p*-toluenesulfonyl or methanesulfonyl groups is rare even in reductions of sugars with lithium aluminum hydride; nonetheless, examples can be found[15,23] when deoxy compounds are formed in low yield as by-products even in those cases where the intramolecular reaction is impossible. In contrast to the preceding ones compound *VIIa* does not exclude the possibility of an intramolecular reaction, and hence the formation of 3-deoxy derivative. In addition to this the substituent in the position 3 of allofuranose derivatives undergoes an S_N2 reaction easily; neither in this case was the formation of any deoxy compound observed in the reduction with Synhydride.

In the reduction of 2,6-bis(*p*-toluene sulfonyl)galactoside *Va* an interruption of the reaction at the proper point made it possible to carry out the reduction to the first step only, and thus obtain the *p*-toluenesulfonyl-6-galactoside *Vb* in good yield. Synhydride attacked the *p*-toluenesulfonyl group in the position 2 preferentially. It is known that during the reduction of compound *Va* with lithium aluminum hydride[24] this reagent reacted with the *p*-toluenesulfonyl group in the position 6 preferentially, and that under splitting of the C—O bond; methyl 6-deoxy-3,4-O-isopropylidene-2-O-*p*-toluenesulfonyl-α-D-galactoside was the reaction product. Hence, in this case the difference between both reagents is observed, both with regard to the relative reaction rate of individual groups in the position 2 and 6, and to the manner of cleavage of the bond (formation of 6-deoxy or 6-hydroxy compounds), because the 6-*p*-toluenesulfonyl group in the case of *galacto*-configuration was split by Synhydride under formation of 6-hydroxy derivatives exclusively.

When comparing the course of the reduction of sugar *p*-toluenesulfonyl esters or methanesulfonyl esters with Synhydride and lithium aluminum hydride, it may be stated that the first reagent enables a safer and more convenient operation, a broader choice of a suitable solvent, and a shorter reaction time. The majority of the reactions is over in 30–60 minutes. On the other hand, the isolation of the products is somewhat more difficult, owing to the presence of methoxyethanol in the reaction mixture. As for the reduction products, in extreme cases both hydrides behave the same, *i.e.* the primary *p*-toluenesulfonyl groups – well accessible and reactive (as in hexofuranoses) – afford deoxy compounds, while the secondary esters – with the exception of intramolecular reductions – are mostly cleaved to hydroxy derivatives. The difference between the two reagents appears in less reactive primary toluenesulfonyl esters (for example *IVa*, *Va*), where lithium aluminum hydride displays a higher tendency to the cleavage of the C—O bond than Synhydride; the ratio

of de oxy to hydroxy compounds in the reaction products is thus higher for reductions with lithium aluminum hydride. A difference is also observed in the relative reaction rates of individual groups, and hence in different products of selective reduction of polysubstituted compounds (as for example *Va*).

EXPERIMENTAL

The solutions were evaporated on a rotatory evaporator at temperatures not exceeding 40°C. For chromatography neutral alumina was used (activity according to Brockmann II—III) or also silica gel L 100—160 μ. The reaction course, purity and the identity of the products were followed by thin-layer chromatography on silica gel G, using the following solvent systems: benzene–ethanol (0—20%), chloroform–methanol (0—20%), ethyl acetate–light petroleum (1 : 2), and benzene–acetone–ethanol (50 : 1 : 1). Detection was carried out by spraying with 2% ceric sulfate in 10% H_2SO_4 and heating. Samples for analysis were dried at room temperature and *in vacuo* (oil pump) for 8 h. The melting points were determined on a Kofler block and they are not corrected. Optical rotations were measured in chloroform solutions of $c = 1 \pm 0{\cdot}1$ concentration.

Substances Used

3-Deoxy-1,2-O-isopropylidene-6-O-*p*-toluenesulfonyl-α-D-*ribo*-hexofuranose (*Ia*), m.p. 48 to 50°C, $[\alpha]_D^{25}$ −4·9°, ref.[16]. 1,2-O-Isopropylidene-6-O-*p*-toluenesulfonyl-α-D-glucofuranose (*Ib*), m.p. 106—107°C, $[\alpha]_D^{20}$ +8·8°, ref.[25]. Methyl 6-O-*p*-toluenesulfonyl-α-D-glucopyranoside (*IIIa*), m.p. 124°C, $[\alpha]_D^{20}$ +98·0°(ethanol), ref.[27]. 1,2 : 3,4-Di-O-isopropylidene-6-O-*p*-toluenesulfonyl-α-D-galactose (*IVa*), m.p. 101—102°C, ref.[28]. Methyl 3,4-O-isopropylidene-2,6-di-O--*p*-toluenesulfonyl-α-D-galactoside (*Va*), m.p. 149—151°C, $[\alpha]_D^{20}$ +114·2° (pyridine), ref.[29]. Methyl 3,4-O-isopropylidene-6-O-*p*-toluenesulfonyl-α-D-galactoside (*Vb*), m.p. 130—131°C, $[\alpha]_D^{20}$ +74·2°, ref.[29]. 3,6-Dideoxy-1,2-O-isopropylidene-5-O-*p*-toluenesulfonyl-α-D-*ribo*-hexofuranose (*VIIIa*), syrup, $[\alpha]_D^{25}$ −87°, ref. [16].

Methyl 2,3-Di-O-methyl-4,6-di-O-*p*-toluenesulfonyl-α-D-glucopyranoside (*IIa*)

Methyl 2,3-di-O-methyl-α-D-glucopyranoside (*IIe*; 2·2 g), prepared by hydrolysis of corresponding 4,6-O-benzylidene derivative[26] with 80% acetic acid, was dissolved in 20 ml of pyridine and a solution of 6 g of *p*-toluenesulfonyl chloride in 20 ml of chloroform was added dropwise and under stirring. After 12 hours' standing the mixture was decomposed with ice and extracted with three 50 ml portions of chloroform. The combined chloroform extracts were washed with dilute hydrochloric acid, sodium hydrogen carbonate solution and water, then evaporated and the residue was crystallized twice from ethanol. Yield 3·9 g (74%) of *IIa*, m.p. 120—122°C, $[\alpha]_D^{20}$ +77·8°. For $C_{23}H_{30}O_{10}S_2$ (530·6) calculated: 52·06% C, 5·70% H, 12·08% S; found: 52·09% C, 5·74% H, 12·17% S.

Methyl 2,3-Di-O-methyl-6-O-*p*-toluenesulfonyl-α-D-glucopyranoside (*IIg*)

A solution of 1·1 g of pyranoside[26] *IIe* was allowed to react with 1,4 g of *p*-toluenesulfonyl chloride in 15 ml of chloroform for 12 h, and the mixture was worked up as in the preceding experiment. A syrup (1·5 g) was obtained which was chromatographed on silica gel to yield

375 mg (14%) of di-*p*-toluenesulfonyl derivative *IIa*, m.p. 120—122°C, and 1 026 mg (56%) of syrupy mono-*p*-toluenesulfonyl derivative *IIg* which was used for methylation without further purification.

Methyl 2,3,4-tri-O-methyl-6-O-*p*-toluenesulfonyl-α-D-glucopyranoside (*IIb*)

The syrupy derivative *IIg* (850 mg) was shaken with 2 g of freshly prepared silver oxide and 2·5 ml of methyl iodide in 10 ml dimethylformamide for 16 h. The mixture was filtered through a layer of supercel, which was then washed with three 40 ml portions of chloroform. The combined filtrates were shaken twice with 50 ml of 1% aqueous sodium cyanide and the aqueous fractions were washed twice with chloroform (20 ml each wash). The combined chloroform fractions were washed with aqueous solution of sodium thiosulfate, dried over magnesium sulfate and evaporated. The residual syrup was chromatographed on silica gel, affording 877 mg of syrupy glucoside *IIb*, $[\alpha]_D^{20}$ +92·8°; for $C_{17}H_{26}O_8S$ (390·5) calculated: 52·29% C, 6·71% H, 8·21% S; found: 52·78% C, 6·90% H, 7·76% S.

1,2 : 5,6-Di-O-isopropylidene-3-O-methanesulfonyl-α-D-allofuranose (*VIa*)

On reaction of 2·6 g of 1,2 : 5,6-di-O-isopropylidene-α-D-allofuranose with 2·3 g of methanesulfonyl chloride in 20 ml of pyridine at 0°C for 24 hours, 3 g (89%) of *VIa*, m.p. 129—130°C, $[\alpha]_D^{20}$ +79·6°, were obtained, in accordance with the literature[30].

1,2-O-Isopropylidene-3-O-methanesulfonyl-α-D-allofuranose (*VIIa*)

This compound was prepared by hydrolysis of diisopropylidene derivative[31] *VIa* (1 g) with 80% acetic acid at 20°C. After the end of the hydrolysis the course of which was followed by thin-layer chromatography the solution was evaporated at 30°C and dried in a vacuum; the syrupy residue (890 mg) was reduced with Synhydride without further purification.

Reduction with Synhydride — Examples of Various Work-ups of the Reaction Mixtures

A) *Decomposition with sodium potassium tartrate*: Synhydride (5 ml) was added to 1 g of galactoside *Va* in 50 ml of benzene and the mixture was refluxed for 1 h. After cooling a solution of 20 g of sodium potassium tartrate in 40 ml of water was added to the mixture under stirring, the benzene layer was separated and the aqueous one extracted with two 50 ml portions of benzene and three 50 ml portions of chloroform. The combined benzene and chloroform extracts were filtered and evaporated and the residue chromatographed on 80 g of alumina. Yield, 48 mg (4·8%) of the starting substance, m.p. 149—150°C, 483 mg (67·4%) of 6-tosylgalactoside *Vb*, m.p. 128—129°C, and 100 mg (23·1%) of galactoside *Vc*, m.p. 102—103°C.

B) *Decomposition with water and alkali*: Compound *IIa* (1 950 mg) in 40 ml benzene was added dropwise to Synhydride (16 ml) in 40 ml of benzene over 10 minutes. The mixture was allowed to stand at 20°C for 1 h and refluxed for another 1 h. After cooling 1 ml of water, 1 ml of 15% sodium hydroxide in water, 15 ml of ether and 3 ml of water[32] were added gradually. The mixture was stirred for 20 min, the clear benzene layer was poured off and the residue was extracted twice with 100 ml of boiling benzene. The filtered benzene extracts were evaporated and the residue chromatographed on alumina, yielding 475 mg (62·5%) of *IIc*, syrup, $[\alpha]_D^{20}$ +136·8°; $C_9H_{18}O_5$ (206·2) (calculated: 52·41% C, 8·79% H; found: 52·46% C, 8·92% H), and 146 mg (17·8%) of *IIe*, m.p. 80—82°C.

C) Decomposition with ethanol and water: Synhydride (2 ml) was added to a solution of 653 mg of syrupy allofuranose *VIIa* (prepared by hydrolysis of *VIa*) in 50 ml of benzene at 60°C, and the mixture was refluxed for 1 h. After cooling 5 ml of ethanol were added, followed by 20 ml water, and both layers formed were filtered and the salts on the filter extracted twice with 50 ml of boiling ethanol. All solutions were evaporated, the residue was extracted four times with 40 ml of methanol, the extract was evaporated and the residue chromatographed on silica gel. Yield 360 mg (75%) of *VIIb*, m.p. 129–131°C.

D) Decomposition with ethanol: Synhydride (3 ml) was added to a solution of *Ia* (1 160 mg) in 25 ml of benzene and the mixture allowed to stand for 30 minutes. After decomposition by addition of 10 ml of ethanol the mixture was diluted with 25 ml of benzene and filtered. The filtrate was evaporated and the residue chromatographed on alumina. Yield 509 mg (83%) of *Ic*, m.p. 37–40°C, $[\alpha]_D^{20}$ −26·8°, identical with the preparate compound described[16].

E) Decomposition with water and isolation by means of ion exchangers: 1 g of solid *IIIa* was added gradually over 1 h to a solution of 6 ml of Synhydride in 100 ml of benzene. After 30 minutes the mixture was decomposed with 100 ml of water, filtered, and the solid residue was extracted with 100 ml of boiling water. The combined aqueous solutions were filtered through a column of 50 ml of Dowex 1X2 and then 50 ml of Wofatit CP 300. The deionized solution was evaporated and a mixture of *IIIb* and *IIIc* obtained, which was separated chromatographically in the form of peracetyl derivatives. Yield 428 mg (50%) of methyl 2,3,4-tri-O-acetyl-6-deoxy-α-D-glucopyranoside, m.p. 56–58°C, further 219 mg (19·5%) of methyl tetra-O-acetyl-α-D-glucopyranoside, m.p. 98–100°C (both are identical with the products isolated in the next experiment), and 20 mg (2%) of methyl 3,6-anhydro-2,4-di-O-acetyl-α-D-glucopyranoside[33], m.p. 127–128°C.

F) Decomposition with ethanol and acetylation of the reaction mixture: A solution of *IIIa* (1 g) in 25 ml of tetrahydrofuran was added dropwise to a solution of Synhydride (6 ml) in 20 ml of tetrahydrofuran and the mixture allowed to stand at 20°C for 12 h. Ethanol (10 ml) was then added and the mixture evaporated in a vacuum. The solid residue was evaporated several times after addition of 50 ml of benzene, then dissolved in 50 ml of warm pyridine, cooled, and mixed with 50 ml of acetic anhydride. After 12 h standing the mixture was poured into 200 ml of icy water and extracted with three 100 ml portions of chloroform. The extract was washed with water, dried over magnesium sulfate, and evaporated. The residue was chromatographed on silica gel to yield: 282 mg (28%) of methyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside[34], m.p. 98–100°C, and 533 mg (61%) of methyl 2,3,4-tri-O-acetyl-6-deoxy-α-D-glucopyranoside, m.p. 56–58°C, $[\alpha]_D^{20}$ +151·3°; literature[35] gives m.p. 78–79°C, $[\alpha]_D$ +153°; for $C_{13}H_{20}O_8$ (304·3) calculated: 51·31% C, 6·62% H; found: 51·45% C, 6·72% H; ^{1}H-NMR spectrum (δ ppm): 5·42 (1 H, m, $J_{2,3}$ = 11·0 Hz, $J_{3,4}$ = 9·5 H, $J_{3,1}$ = 1·5 Hz; H-3), 4·70–4·95 (2 H, m; H-1, H-2), 4·78 (1 H, t, $J_{4,5} = J_{3,4}$ = 9·5 Hz; H-4), 3·86 (1 H, o, $J_{4,5}$ = 9·5 Hz, $J_{5,6}$ = 6·1 Hz; H-5), 3·39 (3 H, s; CH_3O) 2·06, 2·02, 1·99 (3 × 3 H; 3 s; 3 CH_3COO), 1·19 (3 H, d, $J_{5,6}$ = 6·1 Hz; CH_3–C). The spectra were measured on a Varian XL-100 (100 MHz) instrument, in deuteriochloroform, using tetramethylsilane as internal reference.

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REFERENCES

1. Bažant V., Čapka M., Černý M., Chvalovský V., Kochloefl K., Kraus M., Málek J.: Tetrahedron Lett. *1968*, 3303.
2. Černý M., Málek J., Čapka M., Chvalovský V.: This Journal *34*, 1025 (1969).
3. Černý M., Málek J.: This Journal *36*, 2394 (1971).
4. Černý M., Málek J., Čapka M., Chvalovský V.: This Journal *34*, 1033 (1969).
5. Čapka M., Chvalovský V., Kochloefl K., Kraus M.: This Journal *34*, 118 (1969).
6. Corbett J. F.: Chem. Commun. *1968*, 1257.
7. Kraus M., Kochloefl K.: This Journal *34*, 1823 (1969).
8. Jones T. K., Peat J. H. J.: Chem. Ind. (London) *1971*, 995.
9. Causa A. G., Chen. H. Y., Tark S. Y., Harwood H. J.: J. Org. Chem. *38*, 1385 (1973).
10. Čapka M., Chvalovský V., This Journal *34*, 2782 (1969).
11. Časenský B., Macháček J., Abrham K.: This Journal *36*, 2648 (1971).
12. Málek J.: *II. Hydrid-Symposium, Vorträge* p. 239, Goslar 1974.
13. Zobáčová A., Heřmánková V., Jarý J.: This Journal *35*, 327 (1970).
14. Heřmánková V., Zobáčová A., Jarý J.: This Journal *36*, 302 (1971).
15. Zobáčová A., Heřmánková V., Jarý J.: This Journal *36*, 1860 (1971).
16. Zobáčová A., Heřmánková V., Kefurtová Z., Jarý J.: This Journal *40*, 3505 (1975).
17. Schmid H., Karrer P.: Helv. Chim. Acta *32*, 1371 (1949).
18. Wolfrom M. L., Hanessian S.: J. Org. Chem. *27*, 2107 (1962).
19. Brimacombe J. S., Husain A.: J. Chem. Soc. *1967*, 1503.
20. Ball D. H., Parrish F. W.: Advan. Carbohyd. Chem. Biochem. *24*, 143 (1969).
21. Stevens C. L., Blumbergs P., Daniher F. A., Otterbach D. H., Taylor K. G.: J. Org. Chem. *31*, 2823 (1966).
22. Westwood J. H., Chalk R. C., Ball D. H., Long J.: J. Org. Chem. *32*, 1643 (1967).
23. Stevens C. L., Blumbergs P., Otterbach D. H.: J. Org. Chem. *31*, 2817 (1966).
24. Brimacombe J. S., How M. J.: J. Chem. Soc. *1962*, 5037.
25. Szabolcs O., Prey V.: Monatsh. Chem. *88*, 1112 (1957).
26. Eddington R. A., Hirst E. L., Percival E. E.: J. Chem. Soc. *1955*, 2281.
27. Cramer F., Otterbach H., Springmann H.: Chem. Ber. *92*, 384 (1959).
28. Schmidt O. T.: Methods Carbohyd. Chem. *I*, 191 (1962).
29. Rao P. A., Smith F.: J. Chem. Soc. *1944*, 229.
30. Meyer zu Reckendorf W.: Chem. Ber. *101*, 3802 (1968).
31. Collins P. M.: Tetrahedron *21*, 1089 (1965).
32. Mićović V. M., Mihajlović M. L.: J. Org. Chem. *18*, 1190 (1953).
33. Wolfrom M. L., Hung Y. L., Chakravarty P., Yuen G. U., Horton D.: J. Org. Chem. *31*, 2227 (1966).
34. Harris T. L., Hirst E. L., Wood C. E.: J. Chem. Soc. *1932*, 2108.
35. Maclay W. D., Hann R. M., Hudson C. S.: J. Amer. Chem. Soc. *61*, 1660 (1939).

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