SYNTHESIS OF 2,3,5-TRI-O-BENZOYL-D-PENTOFURANOSYL CYANIDES AND THEIR CD SPECTRA

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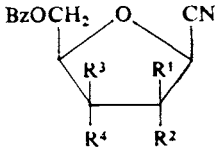
The title compounds *I*—*IV* with the respective *ribo*-, *arabino*-, *xylo*- and *lyxo*-configuration were prepared by reaction of 1-O-acetyl-2,3,5-tri-O-benzoyl-D-pentofuranoses with trimethylsilyl cyanide in 1,2-dichloroethane, catalyzed with tin tetrachloride. The CD spectra of compounds *I*—*IV* and of the conformationally rigid 1,5-anhydro-2,3-di-O-benzoyl-β-D-pentofuranoses *VI*—*VIII* were measured and interpreted by the exciton chirality method.

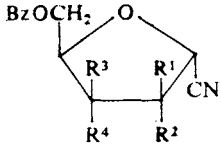
Some time ago we described[1] the preparation of 2,3,5-tri-O-benzoyl-β-D-ribofuranosyl cyanide (*I*) which proved to be a very versatile intermediate in the synthesis of C-nucleosides[2-4]. In connection with the conformational studies of compound *I* by ^{1}H NMR spectroscopy[5] we needed the remaining 2,3,5-tri-O-benzoyl-D-pentofuranosyl cyanides *II*—*IV* with *trans*-configuration at the $C_{(1)}$—$C_{(2)}$ bond and some derivatives of 1,5-anhydro-β-D-pentofuranoses (*VI*—*X*) as models with conformationally fixed furanose ring.

The reaction of acyl halogenoses with mercuric cyanide in nitromethane or acetonitrile represents a general synthesis of *trans*-glycosyl cyanides. This reaction proceeds in 60—80% yields both in the furanosyl (D-*ribo*[1,6], D-*arabino*[7]) and pyranosyl (D-*ribo*[8], D-*xylo*[9], D-*galacto*[10-13], L-*manno*[14]) series, except D-glucopyranose[15] and 2-amino-2-deoxy-D-glucopyranose[16] derivatives; nevertheless, we prepared the compounds *I*—*IV* by reaction of 1-O-acetyl-2,3,5-tri-O-benzoyl-D-pentofuranoses with trimethylsilyl cyanide in 1,2-dichloroethane in the presence of tin tetrachloride, *i.e.* under conditions of the Vorbrüggen nucleoside synthesis[17]. This procedure avoids the preparation of the unstable halogenoses; however, the yields of glycosyl cyanides were only about 45%. After completion of our synthesis of *I*—*IV* two papers appeared which described the preparation of compound *I* by the same reaction in acetonitrile with tin tetrachloride as catalyst[18] or with boron trifluoride etherate without solvent[19] in yields of about 85%. (A mechanistically similar reaction of tert-alkyl chlorides with trimethylsilyl cyanide was performed in dichloromethane with tin chloride as catalyst[20].) For comparison, we prepared the *arabino*-derivative *II* by the mercuric cyanide method according to Barnathan and coworkers[14]. Both

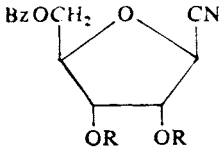
reactions were stereospecific and gave identical *arabino*-derivatives *II*. The β-configuration of compound *I* had been proved in a chemical way already previously[21]. The compounds *II*–*IV* were assigned the *trans*-configuration on the basis of the very probable substitution mechanism involving participation of the acyl group.



I; $R^1 = R^3 = H$, $R^2 = R^4 = OBz$
III; $R^1 = R^4 = H$, $R^2 = R^3 = OBz$



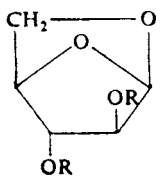
II; $R^2 = R^3 = H$, $R^1 = R^4 = OBz$
IV; $R^2 = R^4 = H$, $R^1 = R^3 = OBz$



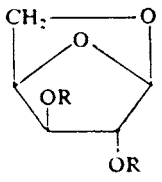
Va; R = H
Vb; 2 R = CO
Vc; 2 R = $C(CH_3)_2$
Vd; 2 R = C_6H_5B
Ve; R = CH_3CO

As models with conformationally fixed furanose ring we prepared derivative of 5-O-benzoyl-β-D-ribofuranosyl cyanide (*Va*), containing fused five-membered rings (2,3-O-carbonate *Vb*, 2,3-O-isopropylidene derivative *Vc*, 2,3-O-benzeneboronate *Vd*), and 1,5-anhydro-β-D-pentofuranose derivatives. The 1,5-anhydro-2,3--di-O-benzoyl-β-D-pentofuranoses *VI*–*VIII* were synthesized by treatment of the corresponding 1,5-anhydro sugars[22] with benzoyl cyanide[23]. 1,5-Anhydro-2,3-O-isopropylidene-β-D-ribofuranose (*IX*) was obtained as a side product in the isopropylidenation of D-ribose[24]. Reaction of 1,5-anhydro-β-D-lyxofuranose with 2,2-dimethoxypropane afforded the already described[22,25] isopropylidene derivative *X*.

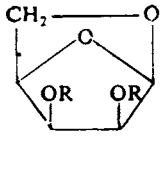
Characteristic CD spectral data (in $\Delta\varepsilon$, $1\ mol^{-1}\ cm^{-1}$) of compounds *I*–*IV* and *VI*–*VIII* are given in Table I; two typical curves are shown in Fig. 1. In the measured spectral region (200–300 nm) the studied compounds show CD bands due to the benzoate chromophore transitions: a very weak multiple band of the aromatic transition B_{2u} in the region 285–260 nm, a strong band at 237–240 nm and a weaker one at 220–223 nm. Both the latter bands can be ascribed to the aromatic transition $B_{1u}(^1L_a)$ of the benzoyl group whose absorption maximum is at 229 to 230 nm (ref.[26]).



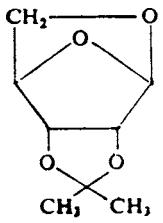
VI; R = Bz



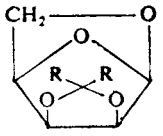
VII; R = Bz



VIII; R = Bz



IX



X; R = CH_3

TABLE I

Circular dichroic data of compounds *I*—*IV*, *Va*—*Ve* and *VI*—*VIII* in ethanol

Compound	Configuration	λ_{max}, nm ($\Delta\varepsilon_{max}$, l mol^{-1} cm^{-1})		A^b
		B_{2u} band[a]	B_{1u} bands	
I	*ribo*	—	237 (+ 8·9) 221 (—2·5)	+11·4
II	*arabino*	+	240 (— 13·9) 223·5 (+1·0)	—14·9
III	*xylo*	+	239·5 (+8·1) 218[c] (0)	+ 8·1
IV	*lyxo*	—	240 (+7·2) 220 (—2·3)	+ 9·5
Va	*ribo*	—	246 (0·61) 222·5 (—0·55)	—
Vb	*ribo*[d]	—	246 (—0·84) 222·5 (+0·75)	—
Vc	*ribo*	—	256(+0·15) 226 (—0·37)	—
Vd	*ribo*[d]	—	243 (—0·26) 228 (+0·78)	—
Ve	*ribo*	—	231·5 (+0·85)	—
VI	*arabino*	+	238 (—27·1) 221·5 (+3·4)	—30·5
VII	*xylo*	—	238 (+30·9) 222 (—2·8)	—32·7
VIII	*lyxo*	+	238[e] (+0·4) —	+ 0·4

[a] The B_{2u} multiple band is in all cases very small, the sign is given only; [b] amplitude $A = \Delta\varepsilon_{max}$ of the long wavelength band minus $\Delta\varepsilon_{max}$ of the short wavelength band; [c] approximate position of a minimum; [d] in acetonitrile; [e] additional band appears at 253 nm ($\Delta\varepsilon$ —0·2).

Circular dichroism of analogous *p*-bromobenzoyl derivatives of pyranoses was studied by Liu and Nakanishi[26]. The interpretation given by these authors is based on the assumption that the optical activity of the aromatic transition $B_{1u}(^1L_a)$ is contributed mainly by mutual interaction of electric transition moments of a pair of identical chromophores[27,28] which splits the dichroic band into two bands of equal intensity and opposite sign (exciton splitting). The sign and magnitude of the bands depend on spatial orientation of the interacting transition moments. Further, if the assumption is valid that the direction of the transition moment B_{1u} of the benzoyl transition essentially parallels the direction of the corresponding C—O bond attached to the saccharide ring, the sign and amplitude of the split band can be correlated with the dihedral angle between these bonds and thus with the configuration or conformation of the saccharide. In all our compounds the dihedral angle in question ($\psi_{2,3}$) is defined by the bonds $O_{(2)}$—$C_{(2)}$—$C_{(3)}$—$O_{(3)}$.

The experimental data of our furanose derivatives show that also their CD spectra are decisively determined by the interaction between the benzoyl chromophores and they can be thus interpreted on the basis of considerations similar to those used for the pyranose series[26]. The observed bands due to the B_{1u} transition differ, however, from the theoretical curves (Fig. 1). As seen, even for a conformationally well defined compound, the long-wavelength lobe (238 nm) of the split band can be one order of magnitude stronger than the short-wavelength one (222 nm), the latter having an almost constant intensity throughout the whole series of compounds. These facts are at variance with the assumed splitting mechanism and the discussion in ref.[27,28] seems to give an only partial explanation.

Concerning the interpretation, the 1,5-anhydro-β-D-pentofuranoses *VI*–*VIII* present no difficulties since their furanose ring is conformationally fixed; according

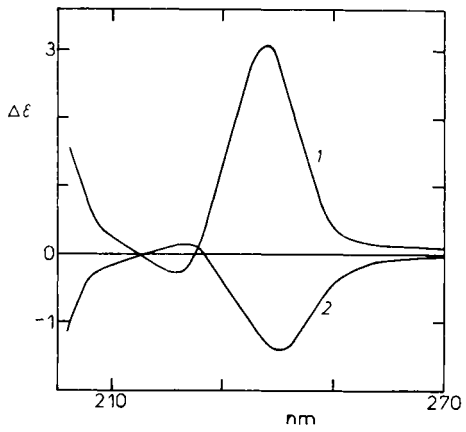


FIG. 1

CD Spectra in ethanol *1* of 1,5-anhydro-2,3-di-O-benzoyl-β-D-xylofuranose (*VII*) and *2* of 2,3,5-tri-O-benzoyl-α-D-arabinofuranosyl cyanide (*II*)

to models we assume the E_0 conformation which agrees also with the ^{1}H NMR spectra of 2,3-di-O-acetyl-1,5-anhydro-β-D-pentofuranoses[22]. In the compound *VI* (*arabino*-configuration) the dihedral angle between the $C_{(2)}$—O and $C_{(3)}$—O bonds has a negative value (on models $\psi_{2,3} - 125°$), the handedness of this arrangemen tbeing negative. The long-wavelength maximum of the B_{1u} band at 238 nm is negative, as predicted theoretically[27,28]. The diastereoisomeric compound *VII* has *xylo*-configuration at the carbon atoms 2 and 3 and the dihedral angle is positive (+125°). The spectrum of *VII* (Fig. 1) is almost completely enantiomorphous with that of compound *VI*. In the *lyxo*-compound *VIII* the mentioned dihedral angle is zero, *i.e.* the molecular segment is achiral. In accord with this fact the CD activity of compound *VIII* is only negligible.

In the case of the cyanides *I*–*IV* (Table I) we must take into consideration that the conformational freedom of their furanose ring is much greater than in compounds *VI*–*VIII* and that other conformations are preferred. The 5-benzoyl group probably does not contribute significantly to the overall dichroism since its position relative to the saccharide ring is in no way stabilized (see low band intensities for the compound *Va*–*Ve* in Table I). The *lyxo*-derivative *IV* exhibits a much higher CD activity than its rigid analogue *VIII*. Its spectrum displays a positive long-wavelength band and resembles (also quantitatively) that of the ribofuranosyl cyanide *I*. Apparently, both compounds exist in forms with the same positive dihedral angle $\psi_{2,3}$ such as in the energetically favourable conformation ^3E or the twisted form $^3T_2$. The spectra of compounds *II* and *III* are similar to those of the rigid analogues *VI* and *VII*; the intensity of the long-wavelength maximum is, however, substantially lower due to the higher conformational flexibility of the furanose ring. The sign of the dihedral angle $O_{(2)}$—$C_{(2)}$—$C_{(3)}$—$O_{(3)}$ is retained but its magnitude is changed by the different conformation of the ring. Here we may find an explanation of the markedly lower amplitude of the *xylo*-derivative *III* relative to the *arabino*-derivative *II*. According to the literature[28], the sign of the B_{1u} band in the spectra of vicinal benzoates does not change in the region of torsion angles 0–180°, the amplitude achieving maximum values at about 70°. We might thus expect a higher absolute value of $\psi_{2,3}$ (farther from the optimum value of 70°) in the *xylo*-derivative *III* than in the rigid analogue *VII* and in the *arabino*-derivative *II*. Such situation would occur if both compounds *II* and *III* existed in conformations with a positive angle $\psi_{2,3}$, *e.g.* in the ^3E form.

Compounds *I*–*IVa*, *VI* and *VIII* were studied also by ^{1}H NMR spectroscopy[5] and the conclusions are in a good agreement with the CD studies even for the conformationally mobile furanosides *I*–*IV*. Both methods indicate that the furanosides *I* and *IV* have a similar dihedral angle $\psi_{2,3}$ and exist as conformational mixtures. For the *ribo*-derivative *I* the ^{1}H NMR study suggests an equimolecular mixture of the ^3E and ^2E forms. Contrary to the ^3E form, the ^2E conformation has a negative torsion angle $\psi_{2,3}$. The CD spectra thus show that either the conformation ^2E is much less

populated or the absolute value of $\psi_{2,3}$ is very low. A similar situation probably exists in the *lyxo*-furanoside *IV*. The $\psi_{2,3}$ values for compounds *II* and *III* (estimated from the dihedral angles $H_{(2)}—C_{(2)}—C_{(3)}—H_{(3)}$ determined by the ^{1}H NMR spectra) are $-145°$ and 180°, respectively, and are in the expected relation; however, for the *xylo*-derivative *III* this value is too high.

Table I also contains data for the *ribo*-derivatives *Va – Ve* with one benzoyl group in position 5. In most cases the aromatic transition B_{1u} manifests itself again as two bands of opposite sign, both of low intensity. This indicates a considerable conformational flexibility of the chain bearing the benzoate chromophore and the presence of at least two types of rotamers about the $C_{(4)}—C_{(5)}$ bond, differing in the band sign. The structural or conformational changes of the *ribo*-furanose ring practically do not affect the conformation of this chain.

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. The analytical samples were dried at 25°C/6·5 Pa for 8 h. The IR spectra were recorded on a UR 20 (Zeiss, Jena) spectrophotometer, optical rotations were measured on a Perkin Elmer 141 polarimeter, CD spectra were taken on a Roussel–Jouan Dichrographe CD 185 Model II in 0·05 – 1·0 cm cells at room temperature; unless stated otherwise, the compounds were measured in ethanol (concentration about 0·2 mg/ml).

Starting Compounds

Trimethylsilyl cyanide was prepared according to Uznanski and Stec[29]. 1-O-Acetyl-2,3,5-tri-O-benzoyl-D-pentofuranoses were prepared by the described procedures (α,β-*arabino*-[30], β-*ribo*-[31], β-*xylo*-[32], *lyxo*-[33]). 1,5-Anhydro-β-D-pentofuranoses of the *arabino*-, *xylo*-, and *lyxo*-configuration were obtained by pyrolysis of the corresponding pentoses[22].

2,3,5-Tri-O-benzoyl-D-pentofuranosyl Cyanides *I – IV*

Tin tetrachloride (0·5 ml) in 1,2-dichloroethane (10 ml) was added dropwise at 0°C to a stirred mixture of 1-O-acetyl-2,3,5-tri-O-benzoyl-D-pentofuranose (1·08 g; 2 mmol) and trimethylsilyl cyanide (0·47 g; 5 mmol) in 1,2-dichloroethane (10 ml) during 10 min. After further 30 min the mixture was set aside for 1 h at room temperature, washed with water (2 × 20 ml), saturated solution of sodium hydrogen carbonate (20 ml), dried over sodium sulfate, and evaporated. The residue was chromatographed on a silica gel column (2 × 40 cm) in benzene–ethyl acetate (20 : 1). The yields, elemental analyses, and physical data are given in Table II.

Preparation of the Cyanide *II* by the "Mercury" Method

Mercuric cyanide (0·75 g; 3·3 mmol; dried at 80°C/6·5 Pa for 8 h) was added at room temperature to a solution of 2,3,5-tri-O-benzoyl-α,β-D-arabinofuranosyl bromide (1·57 g; 3 mmol) in nitromethane (20 ml). The mixture was stirred at room temperature for 8 h, allowed to stand overnight and worked up[1]. The product was chromatographed on a column of silica gel (2 × 40 cm) in toluene–ethyl acetate (10 : 1). Crystallization of the chromatographically homogeneous fraction from ethanol–ether (10 : 1) at 0°C overnight afforded 1·21 g (86%) of compound *II*, melting

at 72–73°C. An analytical sample, recrystallized from the same mixture, melted at 73–74°C. When heated slowly above the melting point, the melt crystallized and remelted at 102–103°C. This higher-melting modification was obtained by crystallization of the lower-melting form from ether–light petroleum; m.p. 103–104°C. Chloroform solutions of both forms had identical IR spectra; $[\alpha]_D^{25}$ −20·5° (*c* 0·5; chloroform). Reported[7] m.p. 80°C and $[\alpha]_D^{25}$ −23·8° (*c* 0·16, chloroform).

5-O-Benzoyl-β-D-ribofuranosyl Cyanide 2,3-O-Carbonate (*Vb*)

Pyridine (2 ml) was added to a solution of 5-O-benzoyl-β-D-ribofuranosyl cyanide[21] (*Va*; 0·26 g) in chloroform (15 ml). After cooling in an ice bath, a 30% fosgen solution in chloroform (1·5 ml) was added with stirring, the mixture was left aside for 1·5 h in the ice bath, washed with water and twice with 10% phosphoric acid. After drying over sodium sulfate, the solvent was evaporated, the residue chromatographed on silica gel in toluene–methyl acetate (2 : 1) and the product crystallized from ethanol; yield 0·21 g (74%), m.p. 157–158°C (ethanol). The analytical sample was sublimed at 160°C/2 Pa. For $C_{14}H_{11}NO_6$ (289·2) calculated: 58·13% C, 3·83% H, 4·84% N; found: 58·03% C, 3·74% H, 4·79% N.

TABLE II

2,3,5-Tri-O-benzoyl-D-pentofuranosyl cyanides *I*–*IV* and 1,5-anhydro-2,3-di-O-benzoyl-β-D-pentofuranoses *VI*–*VIII*

Compound Configuration	Yield, % m.p., °C[a]	$[\alpha]_D^{25}$ (*c*, $CHCl_3$)	IR-Bands of CN in cm^{-1} (CCl_4)
I	43	+23·8°	2 370, 2 350
ribo	(80–81)	(0·5)	2 331
II[b]	48	−21·6°	2 376
arabino	(73–74)	(0·5)	
III[c]	35	+54·1°	2 376, 2 352
xylo	(98)	(0·5)	
IV[d]	41	+33·0°	2 374, 2 350
lyxo	(104–105)	(0·2)	
VI[e]	57	+273°	–
arabino	(124–125)[f]	(0·5)	
VII[g]	76	+151°	–
xylo	(81)	(0·5)	
VIII[h]	68	−79·2°	–
lyxo	(65–60)[i]	(0·3)	

[a] Crystallized from ethanol–ether (95 : 5); [b] for $C_{27}H_{21}NO_7$ (471·45) calculated: 68·78% C, 4·49% H, 2·97% N; found: 68·53% C, 4·33% H, 2·62% N; [c] 68·48% C, 4·41% H, 2·99% N; [d] 68·70% C, 4·45% H, 3·02% N; [e] for $C_{19}H_{16}O_6$ (340·3) calculated: 67·05% C, 4·74% H; found: 67·13% C, 4·97% H; [f] from ethanol; [g] 67·15% C, 5·08% H; [h] 67·25% C, 4·75% H; [i] from methanol.

5-O-Benzoyl-2,3-O-isopropylidene-β-D-ribofuranosyl Cyanide (*Vc*)

A 5% solution of hydrogen chloride in dioxane (0·2 ml) was added at room temperature to a stirred suspension of compound *Va* (300 mg) in a mixture of 2,2-dimethoxypropane (3 ml) and acetone (3 ml). After dissolution, the mixture was allowed to stand for 1 h at room temperature, neutralized with triethylamine (0·1 ml) and taken down. The residue was dissolved in ether, triethylamine hydrochloride was filtered off, the filtrate was evaporated and chromatographed on a column of silica gel (2 × 25 cm) in toluene–ether (5 : 1), affording 120 mg (35%) of *Vc*, m.p. 56°C (ether–light petroleum). For $C_{16}H_{17}NO_5$ (303·3) calculated: 63·35% C, 5·65% H, 4·62% N; found: 63·34% C, 5·57% H, 4·25% N.

5-O-Benzoyl-β-D-ribofuranosyl Cyanide 2,3-O-Benzeneboronate (*Vd*)

A mixture of compound *Va* (0·263 g; 1 mmol) and benzeneboronic acid (0·134 g; 1·1 mmol) was suspended in benzene (50 ml). Half of the solvent was distilled from the stirred mixture under ordinary pressure during 1 h. Addition of n-hexane (10 ml) precipitated the benzeneboronate *Vd* (0·28 g; 80%), m.p. 102—103°C, which was not purified further; $[\alpha]_D^{25}$ +19·4° (*c* 0·5; $CHCl_3$). An attempted chromatography on silica gel resulted in hydrolytic decomposition. For $C_{19}H_{16}BNO_5$ (349·2) calculated: 65·36% C, 4·62% H, 4·01% N; found: 65·92% C, 4·64% H, 3·87% N. Mass spectrum related to ^{11}B, *m/z*: 349 (M^+), 293 (M^+—CH(OH)CN), 227 (M^+—C_6H_5COOH).

2,3-Di-O-acetyl-5-O-benzoyl-β-D-ribofuranosyl Cyanide (*Ve*)

A solution of compound *Va* (0·26 g) in a mixture of pyridine (2 ml) and acetic anhydride (1 ml) was set aside for 12 h at room temperature. Ethanol (10 ml) was added and after 1 h the mixture was evaporated. The residue was codistilled with toluene (3 × 15 ml) *in vacuo* and chromatographed on silica gel in n-hexane–ethyl acetate (1 : 1); yield 0·31 g (89%). An analytical sample of *Ve* was rechromatographed (HPLC) in the above-mentioned system and the sirupy residue was dried at 70°C/2·6 Pa for 5 h. For $C_{17}H_{17}NO_7$ (347·3) calculated: 58·79% C, 4·93% H, 4·03% N; found: 59·00% C, 4·96% H, 3·86% N.

1,5-Anhydro-2,3-di-O-benzoyl-β-D-pentofuranoses *VI*—*VIII*

Triethylamine (0·2 ml) was added to a mixture of 1,5-anhydro-D-pentofuranose (0·264 g; 2 mmol) and benzoyl cyanide (0·655 g; 5 mmol) in acetonitrile (10 ml). After standing at room temperature overnight, the solvent was evaporated and the residue chromatographed on a silica gel column in toluene–ethyl acetate (20 : 1). The yields, melting points and elemental analyses are given in Table II.

1,5-Anhydro-2,3-O-isopropylidene-β-D-ribofuranose (*IX*)

The title compound was obtained as a side product in the isopropylidenation of D-ribose according to Levene[24]. The lower-boiling solid fraction obtained by distillation of the reaction mixture *in vacuo* was crystallized from methanol, m.p. 59—60°C, $[\alpha]_D^{25}$ −69·2° (*c* 0·6; methanol), reported[24] m.p. 60—61°C, $[\alpha]_D^{25}$ −64·3° (methanol).

1,5-Anhydro-2,3-O-isopropylidene-β-D-lyxofuranose (*X*)

1,5-Anhydro-β-D-lyxofuranose (100 mg) was converted to the compound *X* as described for the compound *Vc*. Crystallization of the crude product from n-hexane–ether afforded 85 mg (65%) of

X, m.p. 69–70°C; $[\alpha]_D^{25}$ −104° (*c* 0·4; acetone); reported[25] m.p. 69–70°C and $[\alpha]_D^{25}$ −102° (*c* 0·5; acetone). The analytical sample was sublimed at 70°C/6·5 Pa. Mass spectrum, *m/z*: 172 (M^+), 157 (M^+-15), 143, 126, 114 ($M^+-CH_3COCH_3$), 85, 60, 59, 43. The fragmentation is in accord with that given in ref.[25].

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