THE STRUCTURE OF ACETOMYCIN

SPECTROSCOPIC CHARACTERIZATION AND X-RAY ANALYSIS OF A BROMO DERIVATIVE

HERMANN UHR and AXEL ZEECK*

Institut für Organische Chemie der Universität,
Tammannstr. 2, D-3400 Göttingen, F.R.G.

WILLIAM CLEGG and ERNST EGERT

Institut für Anorganische Chemie der Universität,
Tammannstr. 4, D-3400 Göttingen, F.R.G.

HERMANN FUHRER and HEINRICH H. PETER

Ciba-Geigy AG, CH-4002 Basel, Switzerland

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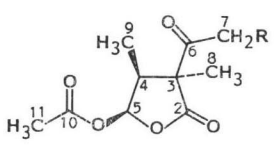
Acetomycin (**1a**), known since 1958, has been further characterized by NMR and CD spectra. The 3-acetyl side chain of **1a** is reduced selectively by sodium cyanoborohydride yielding the diastereomeric alcohols **2a** and **3a**, which were esterified to the crystalline bromoacetates **2c** and **3c**. The structure and absolute configuration of **3c** was determined by X-ray analysis. From these data the absolute configuration of **1a** followed as 3*S*, 4*S*, 5*R*.

Acetomycin (**1a**) is produced by *Streptomyces ramulosus* (TÜ 34 = ETH 17653) as a main component[1]. In the course of chemical screening several other metabolites like β-oxotryptamines and new antibiotics of the amicetin group were extracted from the culture broth[2,3]. The constitution of **1a** was determined in 1958 and was a highly substituted γ-lactone[4], but for structure-activity relationships and synthesis design, a knowledge of the absolute configuration is necessary. In this paper we report on the supplementary physico-chemical characterization, derivatization of the 3-acetyl side chain and the determination of the absolute crystal structure of a bromine-containing derivative.

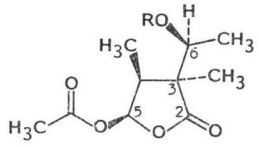
Characterization and Derivatives

Acetomycin was crystallized from methanol or ether - pentane (1 : 1). On TLC (Rf values see Table 1) **1a** and its derivatives gave orange spots with vanillin-H_2SO_4; with amino acids an orange to

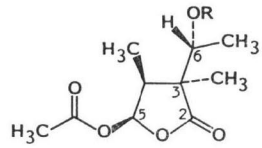
Scheme 1.



1a R=H
1b R=Br



2a ~ c



3a ~ c

a R=H
b R=$\overset{12}{C}O\overset{13}{C}H_3$
c R=$\overset{12}{C}O\overset{13}{C}H_2Br$

Table 1. Rf values of acetomycin (**1a**) and its derivatives on silica gel TLC plates[a].

Solvent system	1a	1b	2a	3a	2b	3b	2c	3c
$CHCl_3$ - MeOH (98: 2)	0.49	0.57	0.26	0.19	0.46	0.51	0.48	0.51
Ether - pentane (1: 2)	0.22	0.23	0.09	0.07	0.16	0.21	0.20	0.23

[a] Detection by color reaction with vanillin-sulfuric acid.

violet color was observed.

The optical rotation is $[\alpha]_D^{20}$ −157° (*c* 1.25, ethanol). The CD-spectrum shows weak Cotton effects between 280 and 320 nm and a maximum at 216 nm ($[\theta]^{25}$ +2,340). In the EI-mass spectrum the molecular ion (expected at *m/z* 214, $C_{10}H_{14}O_5$) is not observable. Key fragments are *m/z* 172 (M−42), 155/154 (M−59/M−60), 83, 55 and the basic peak at *m/z* 43. The assignment of ^1H NMR signals succeeded using both δ values and coupling constants (Table 2). The vicinal coupling between 4-H and 5-H presumed a *cis*-configuration for these protons[5]. $^1H/^{13}C$ Hetero decoupling experiments proved the assignment of the methyl signals in the ^{13}C NMR spectrum. A remarkable high-field shift of the 9-methyl group suggested that it was *cis* to both the adjacent acetyl and acetoxy groups.

Since suitable crystals of **1a** were not available, we decided to synthesize and crystallize a bromine-containing derivative in order to determine the absolute configuration. The bromination of **1a** was accomplished with bromine in glacial acetic acid and gave the 7-bromo derivative **1b**. However, crystals of **1b** obtained from ether - *n*-hexane (1: 1) were not suitable for X-ray analysis. The selective reduction of the carbonyl group in the acetyl side chain to a secondary alcohol was achieved by treatment with sodium cyanoborohydride[6] in methanol at pH 3. The dihydro derivative (69% yield) was separated into the diastereomers **2a** and **3a** by chromatography on silica gel; **2a** and **3a** were later determined as the 6*S* and 6*R* derivative, respectively. The ketone absorption in the IR spectrum of **1a** is lacking in **2a** and **3a**. In the ^1H NMR spectrum the signal of the 7-methyl group shifts to high field and is now observable as a doublet at δ 1.28 (J=6.2 Hz) in **2a** or 1.34 (J=6.5 Hz) in **3a**.

The hydroxyl group was esterified by treatment of a mixture **2a**/**3a** with acetic anhydride-sodium acetate at 60°C and the resulting diastereomeric acetates **2b** and **3b** separated on silica gel in ratio 1: 1. Their constitutions were derived from spectroscopic data. Noteworthy is the difference of the coupling constants between 5-H and 4-H in the ^1H NMR spectrum (Table 3). Thus the stereochemistry of the acetoxy ethyl side-chain at C-3 seems to influence the conformation of the lactone ring, which shows that it can be dangerous to deduce the relative configuration of a highly substituted γ-lactone from

Table 2. NMR data of acetomycin (**1a**) in $CDCl_3$ (δ values in ppm).

Position	^1H NMR (100 MHz)	^{13}C NMR (25.2 MHz)
2	—	177.0 s
3	—	57.0 s
4	2.60 dq	45.5 d
5	6.59 d (J=5.0 Hz)	94.1 d
6	—	203.3 s
7	2.30 s	28.9 q
8	1.43 s	21.0 q
9	1.07 d (J=7.4 Hz)	9.4 q
10	—	168.6 s
11	2.10 s	20.6 q

Table 3. δ values (ppm) and coupling constants of the vicinal H-atoms at the lactone ring of acetomycin (**1a**) and its diastereomeric derivatives ($CDCl_3$, 80 MHz).

Compound	4-H	5-H	J (Hz)
1a	2.60	6.59	5.0
2a	2.55	6.55	6.0
3a	2.53	6.49	5.8
2b	2.57	6.51	6.7
3b	2.46	6.45	5.2
2c	2.58	6.51	6.4
3c	2.48	6.47	5.4

coupling constants of vicinal H-atoms. Esterification with bromoacetyl bromide in dry carbon tetrachloride yielded **2c** and **3c**, which were then separated analogously to **2b**/**3b**. With respect to the assignment of the dihydro derivatives **2a** and **3a** to the corresponding acetates and bromoacetates by Rf relation, it is remarkable that the faster running alcohol (**2a**) yielded the slower running acetate (**2b**) and bromoacetate (**2c**).

Crystal Structure of **3c**

The structure determination of **3c** is rather accurate as can be seen from the low standard deviations of bond lengths and angles (data deposited). The absolute configuration was unequivocally determined as 3*S*,4*S*,5*R*,6*R* by making use of the anomalous scattering of the bromine atom; the absolute configuration of acetomycin and its derivatives can readily be deduced therefrom. The molecular geometry is characterized by steric crowding of the substituents on one side of the lactone ring (Fig. 1). The latter has an envelope conformation with C-4 out of plane, which gives rise to torsion angles of 38 and $-42°$ between C-6 and C-9, and C-9 and O-5, respectively. The substituents at C-3 and C-5 form *trans* chains from C-2 to Br and from C-4 to C-11 with torsion angles ranging from 153 to 180°.

After the completion of this work it came to our notice that F. H. CANO and C. FOCES-FOCES have recently solved the structure of acetomycin by X-ray analysis with results consistent with ours[7].

Fig. 1. Perspective view of **3c** with oxygen atoms shaded.

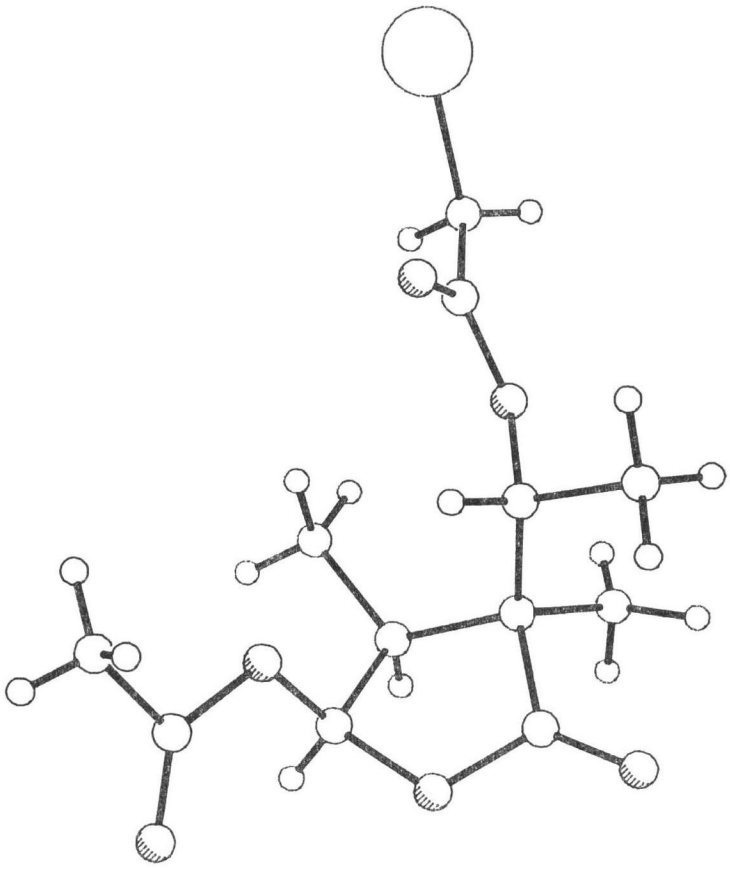


Table 4. Antimicrobial activity of acetomycin (agar diffusion method, 6 mm paper disk, inhibitory diameter in mm).

Test organism	10 mg/ml	1 mg/ml	0.1 mg/ml
Bacillus subtilis	12/24 p	7/9 p	—
Staphylococcus aureus	9/15 p	—	—
S. aureus 2999 (penicillin resistant)	8/16 p	—	—
Streptococcus faecalis	—	—	—
Neisseria catarrhalis	7	—	—
Alcaligenes faecalis	9	—	—
Escherichia coli	—	—	—
Proteus vulgaris	—	—	—
Klebsiella pneumoniae	—	—	—
Pseudomonas aeruginosa	—	—	—
Streptomyces viridochromogenes	22/34 p	12 p	—
Candida albicans	7	—	—
Saccharomyces cerevisiae	15	10 p	—
Trichophyton mentagrophytes	11/28 p	11 p	—
Piricularia oryzae	23/35 p	16/20 p	10 p
Botrytis cinerea	12	—	—

p: Partial (single colonies within the inhibition zone).

Discussion

Acetomycin represents a unique type among the known antibiotics. The density of the three adjacent chiral centers at the lactone ring-system is remarkable. The polar groups are arranged on one side of the molecule. The acetoxy instead of a hydroxyl group is necessary to avoid racemization by ring-chain tautomerism and the methyl group at C-3 prevents racemization of the β-ketoester. Thus nature utilized the smallest substituents in order to fix the structure.

In the biosynthesis of acetomycin the origin of C-6/C-7, C-10/C-11 and C-2/C-3 is acetate, the methyl group at C-3 results from L-methionine and C-9/C-4/C-5 is built up by a C_3-unit from D-glucose[8].

1a shows inhibitory effects (*in vitro*) on Gram-positive bacteria, some fungi and protozoae[1] (additional data see Table 4). The tube dilution test gave the following MIC: *Bacillus subtilis* 30~60 μg/ml, *Mycobacterium tuberculosis* 3 μg/ml and *Trichomonas foetus* 10 μg/ml. The biological activity disappears after reduction of 6-CO; the alcohols **2a** and **3a** as well as their acetates **2b** and **3b** are inactive.

Experimental

General

IR spectra in pressed KBr disks were recorded using a Perkin-Elmer model 297 spectrometer. ^{1}H NMR spectra were determined at 80 MHz with a Varian FT-80, at 100 MHz with a Varian XL-100 or at 200 MHz with a Varian XL-200. ^{13}C NMR spectra were obtained on a Varian FT-80 (20.1 MHz), a Varian XL-100 (25.2 MHz) or a Varian XL-200 (50.4 MHz). Chemical shifts (δ in ppm) are reported relative to internal TMS. EI-mass spectra were taken with a Varian MAT-731 instrument (70 eV). Optical rotations were recorded with a Perkin-Elmer model 241 polarimeter. CD-spectra were determined with a Jasco J 500 A. The separation of diastereomers was carried out by chromatography on a Lobar-column size C (Merck, Darmstadt) and a ISCO metering pump model 310 (flow rate: 100 ml/hour). Thin-layer chromatograpy (TLC) was performed on silica gel (Machery & Nagel, SIL G-100 UV_{254}, 20×20 cm, 0.25 mm).

(3*S*,4*S*,5*R*)-5-Acetoxy-3-acetyl-3,4-dimethyltetrahydrofuran-2-one (Acetomycin, **1a**)

^{1}H and ^{13}C NMR spectra; see Table 2; EI-MS *m/z* (abundant) 172 (3%, M−42), 155 (1%, M−

59), 154 (3%, M−60), 113 (6%), 112 (32%), 111 (12%), 101 (5%), 99 (5%), 98 (3%), 84 (5%), 83 (61%), 55 (21%), 43 (100%); CD λ_{max}^{MeOH} nm ([θ]^{25}) 317 (+58), 311 (−58), 305 (+58), 299 (−102), 295 (0), 289 (−147), 285 (−100), 281 (−146), 216 (+2,340).

(3*S*,4*S*,5*R*)-5-Acetoxy-3-bromoacetyl-3,4-dimethyltetrahydrofuran-2-one (**1b**)

A solution of 55 mg Br_2 (0.35 mmol) in 4.5 ml acetic acid was added dropwise to a solution of 74 mg (0.35 mmol) **1a** in 10 ml glacial acetic acid/1 drop 45% HBr and stirred at room temp for 1 hour. The reaction mixture was evaporated *in vacuo* and the residue chromatographed on a silica gel column (28×1 cm) with $CHCl_3$ - MeOH (99: 1) as eluant. The first fraction gave 75 mg (73%) **1b** followed by 8 mg (11%) recovered **1a**. **1b** was recrystallized from ether - *n*-hexane (1: 1): mp 48°C; Rf see Table 1; $[\alpha]_D^{20}$ −132° (*c* 1.1, EtOH); IR cm^{-1} 1792 (s), 1768 (s), 1730 (s); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.06 (d, *J*=7.3 Hz, 9-H_3), 1.52 (s, 8-H_3), 2.13 (s, 11-H_3), 2.56 (dq, *J*=5.3 and 7.3 Hz, 4-H), 4.29 (s, 7-H_2), 6.55 (d, *J*=5.3 Hz, 5-H); EI-MS *m/z* (abundant) 252/250 (0.4%, M−42), 199 (3%), 191/189 (5%), 172 (7%), 123/121 (4%), 112 (57%), 83 (71%), 55 (17%), 43 (100%).

Anal Calcd for $C_{10}H_{13}O_5Br$: C 40.98, H 4.47, Br 27.27.
Found: C 40.07, H 4.14, Br 28.02.

Reduction of Acetomycin (**1a**)

170 mg sodium cyanoborohydride were added to a solution of 424 mg **1a** in MeOH and stirred at room temp. Dropwise addition of 1 M HCl kept the solution at pH 3 (indicator; methyl orange). During the next 3 days 4 portions of 20 mg reagent were added. The reaction mixture was evaporated to dryness, dissolved in water and extracted with ether. The residue after drying and evaporating was chromatographed on a silica gel column (35×1.5 cm, $CHCl_3$ - MeOH (98: 2)) and then eluated yielding 93 mg (22%) **1a** and 191 mg (68%) dihydroacetomycin (**2a**/**3a**). The mixture of the diastereomers **2a**/**3a** was separated on silica gel (Lobar-column, $CHCl_3$). The eluants contained 124 mg pure **2a**, 10 mg **2a**/**3a** (mixture) and 138 mg pure **3a**.

(3*S*,4*S*,5*R*,6*S*)-5-Acetoxy-3-(1-hydroxyethyl)-3,4-dimethyltetrahydrofuran-2-one (**2a**) eluated first was oily. Rf value see Table 1; $[\alpha]_D^{20}$ −99° (*c* 0.44, EtOH); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.11 (d, *J*=7.5 Hz, 9-H_3), 1.28 (d, *J*=6.2 Hz, 7-H_3), 1.30 (s, 8-H_3), 2.16 (s, 11-H_3), 2.55 (dq, *J*=6.0 and 7.5 Hz, 4-H), 2.90 (br, 6-OH), 3.99 (dq, *J*=6.2 and 2.4 Hz, 6-H), 6.55 (d, *J*=6.0 Hz, 5-H); EI-MS *m/z* (abundant) 172 (2%), 157 (3%), 130 (3%), 112 (64%), 101 (11%), 83 (69%), 69 (8%), 55 (28%), 43 (100%).

Anal Calcd for $C_{10}H_{16}O_5$: C 55.55, H 7.46.
Found: C 55.62, H 7.42.

The slower running substance **3a** (6*R* diastereomer of **2a**) was recrystallized from ether - petroleum ether (3: 1) as colorless needles: mp 63°C; Rf see Table 1; $[\alpha]_D^{20}$ −144° (*c* 0.71, EtOH); IR cm^{-1} 1792 (s), 1735 (s); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.18 (d, *J*=7.4 Hz, 9-H_3), 1.30 (s, 8-H_3), 1.34 (d, *J*=6.5 Hz, 7-H_3), 1.65 (s, 6-OH), 2.14 (s, 11-H_3), 2.53 (dq, *J*=5.8 and 7.4 Hz, 4-H), 4.14 (q, *J*=6.5 Hz, 6-H), 6.49 (d, *J*=5.8 Hz, 5-H); ^{13}C NMR (50.4 MHz, $CDCl_3$) δ 178.88 (C-2), 169.10 (C-10), 94.12 (C-5), 68.10 (C-6), 48.80 (C-3), 44.44 (C-4), 20.89/20.03/17.92 (C-11/C-8/C-7), 9.14 (C-9); EI-MS *m/z* (abundant) 199 (0.2%), 172 (5%), 157 (4%), 130 (4%), 112 (100%), 101 (14%), 83 (77%), 69 (7%), 55 (18%), 43 (81%).

Anal Calcd for $C_{10}H_{16}O_5$: C 55.55, H 7.46.
Found: C 55.73, H 7.34.

5-Acetoxy-3-(1-acetoxyethyl)-3,4-dimethyltetrahydrofuran-2-one (**2b** and **3b**)

195 mg of a **2a**/**3a** containing mixture was dissolved in a suspension of 3 ml acetic anhydride and 300 mg sodium acetate and stirred at 60°C for 6 hours. The reaction mixture was poured into 8 g ice-water, stirred for 2 hours and extracted with ether. The organic layer was washed with H_2O, dried and evaporated to dryness. The residue was chromatographed on a column (silica gel, 35× 1.5 cm) with $CHCl_3$ - MeOH (98: 2). The main fraction gave a mixture of 175 mg (75%) **2b**/**3b**. The diastereomers were separated on silica gel (Lobar-column) with $CHCl_3$ - petroleum ether (5: 1). The eluant was controlled by TLC. The first fraction contained 80 mg **3b**, the second 88 mg **2b**.

(3*S*,4*S*,5*R*,6*S*)-Epimer **2b**: MP 117~119°C; Rf see Table 1; $[\alpha]_D^{20}$ −87° (*c* 0.83, EtOH); IR cm^{-1} 1781 (s), 1754 (s), 1729 (s); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.04 (d, *J*=7.4 Hz, 9-H_3), 1.28 (s, 8-H_3),

1.35 (d, J=6.4 Hz, 7-H_3), 2.07 (s, 13-H_3), 2.14 (s, 11-H_3), 2.57 (m, 4-H), 5.06 (q, J=6.4 Hz, 6-H), 6.51 (d, J=6.7 Hz, 5-H); ^{13}C NMR (20.1 MHz, $CDCl_3$) δ 177.31 (C-2), 169.73/169.29 (C-10/C-12), 93.44 (C-5), 70.25 (C-6), 46.51 (C-3), 43.90 (C-4), 21.47/21.38/20.90/15.83 (C-13/C-11/C-8/C-7), 8.42 (C-9); EI-MS m/z (abundant) 214 (1%), 199 (2%), 172 (4%), 157 (11%), 154 (9%), 112 (49%), 83 (56%), 43 (100%).

Anal Calcd for $C_{12}H_{18}O_6$: C 55.81, H 7.02.
Found: C 55.72, H 7.05.

(3*S*,4*S*,5*R*,6*R*)-Epimer **3b**: MP 114°C; Rf see Table 1; $[\alpha]_D^{20}$ −127° (c 0.85, EtOH); IR cm^{-1} 1781 (s), 1752 (s), 1735 (s); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.02 (d, J=7.4 Hz, 9-H_3), 1.28 (d, J=6.3 Hz, 7-H_3), 1.35 (s, 8-H_3), 2.03 (s, 13-H_3), 2.14 (s, 11-H_3), 2.46 (dq, J=5.2 and 7.4 Hz, 4-H), 5.33 (q, J=6.3 Hz, 6-H), 6.45 (d, J=5.2 Hz, 5-H); EI-MS m/z (abundant) 214 (1%), 199 (1%), 172 (2%), 157 (6%), 154 (6%), 112 (28%), 83 (42%), 43 (100%).

Anal Calcd for $C_{12}H_{18}O_6$: C 55.81, H 7.02.
Found: C 55.74, H 7.06.

Relation of **2a** and **2b** by Rf-comparison: 10 mg pure **2a** were acetylated as described above. The isolated acetate was compared with pure **2b** and **3b** on silica gel TLC plates (20×20 cm) with $CHCl_3$ - MeOH (98: 2). The zones became visible after spotting with vanillin-H_2SO_4 (Rf values see Table 1).

5-Acetoxy-3-(1-bromoacetoxyethyl)-3,4-dimethyltetrahydrofuran-2-one (**2c** and **3c**)

A solution of 200 mg (0.93 mmol) **2a**/**3a** (1: 1) in carbon tetrachloride was stirred for 4.5 hours after addition of 360 mg (1.8 mmol) bromoacetyl bromide. The reaction mixture was poured into 10 g ice-water, stirred for 2 hours followed by extraction with $CHCl_3$. The organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography on a silica gel column (35×1.5 cm, $CHCl_3$ - MeOH (98: 2)) and gave 204 mg (65%) of the diastereomers **2c**/**3c**. A separation of the diastereomers was carried out with 150 mg by chromatography on silica gel (Lobar-column, $CHCl_3$). The fractionated zones were controlled by TLC. The first fraction gave 56 mg **3c** followed by 75 mg **2c**. The bromoacetates were recrystallized from ether - n-hexane (1: 1).

(3*S*,4*S*,5*R*,6*S*)-Epimer **2c**: MP 115°C; Rf value see Table 1; $[\alpha]_D^{20}$ −80° (c 0.99, EtOH); IR cm^{-1} 1778 (s), 1764 (s), 1737 (s); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.07 (d, J=7.5 Hz, 9-H_3), 1.31 (s, 8-H_3), 1.38 (d, J=6.4 Hz, 7-H_3), 2.16 (s, 11-H_3), 2.58 (dq, J=6.4 and 7.5 Hz, 4-H), 3.84 (s, 13-H_2), 5.19 (q, J=6.4 Hz, 6-H), 6.51 (d, J=6.4 Hz, 5-H); ^{13}C NMR (20.1 MHz, $CDCl_3$) δ 176.89 (C-2), 169.17 (C-10), 166.03 (C-12), 93.49 (C-5), 72.20 (C-6), 46.72/43.94 (C-3/C-4), 26.08 (C-13), 21.07/20.96/15.83 (C-11/C-8/C-7), 8.72 (C-9); EI-MS m/z (abundant) 279/277 (2%, M−59), 234/232 (2%), 172 (4%), 157 (8%), 154 (8%), 112 (61%), 111 (25%), 97 (32%), 83 (87%), 55 (22%), 43 (100%); CD λ_{max}^{MeOH} nm ($[\theta]^{25}$) 231 (−4,585).

Anal Calcd for $C_{12}H_{17}O_6Br$: C 42.75, H 5.08, Br 23.70.
Found: C 42.81, H 5.03, Br 23.86.

(3*S*,4*S*,5*R*,6*R*)-Epimer **3c**: MP 122°C; Rf see Table 1; $[\alpha]_D^{20}$ −109° (c 0.82, EtOH); IR cm^{-1} 1780 (s), 1759 (s), 1750 (s); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.05 (d, J=7.5 Hz, 9-H_3), 1.33 (d, J=6.4 Hz, 7-H_3), 1.37 (s, 8-H_3), 2.15 (s, 11-H_3), 2.48 (dq, J=5.4 and 7.5 Hz, 4-H), 3.80 (s, 13-H_2), 5.39 (q, J=6.4 Hz, 6-H), 6.47 (d, J=5.4 Hz, 5-H); ^{13}C NMR (20.1 MHz, $CDCl_3$) δ 176.84 (C-2), 169.02 (C-10), 165.85 (C-12), 93.94 (C-5), 71.80 (C-6), 47.49/44.76 (C-3/C-4), 25.75 (C-13), 20.82/17.45/16.08 (C-11/C-8/C-7), 8.81 (C-9); EI-MS m/z (abundant) 279/277 (2%, M−59), 234/232 (2%), 157 (11%), 112 (62%), 111 (28%), 97 (29%), 87 (71%), 55 (27%), 43 (100%); CD λ_{max}^{MeOH} nm ($[\theta]^{25}$) 243 (+423), 219 (−595).

Anal Calcd for $C_{12}H_{17}O_6Br$: C 42.75, H 5.08, Br 23.70.
Found: C 42.53, H 5.13, Br 23.37.

Relation of **2a** and **2c** by Rf-comparison: 10 mg pure **2a** were dissolved in 0.5 ml carbon tetrachloride and reacted with bromoacetyl bromide as described above. The isolated bromoacetate was compared with pure **2c** and **3c** (see Table 1).

X-Ray Analysis of **3c**

3c (molecular formula: $C_{12}H_{17}BrO_6$, M_r=337.2) was crystallized by liquid diffusion of pentane into EtOH - CH_2Cl_2 (98: 2). Crystal size 0.6×0.4×0.2 mm, orthorhombic, space group $P2_12_12_1$, a=984.6 (1), b=1096.2 (1), c=1341.6 (1) pm, U=1.448 nm^3, Z=4, D_c=1.546 g·cm^{-3}, μ(Mo-K_α)=

2.83 mm^{-1}, Stoe four-circle diffractometer, data collection with profile-fitting method[9], $2\theta_{max}=60°$, 3,419 unique reflections including Friedel opposites (measured at -2θ, $\omega-2\theta$, χ, Φ in order to reduce systematic errors), 2,850 with $|F|>3\sigma_F$ treated as observed, empirical absorption correction ($R_{int}=0.013$ for 317 azimuthal-scan data), structure solved by Patterson and Fourier techniques, all H atoms located by difference electron-density synthesis and refined with fixed individual temperature factors, anisotropic refinement with weights $w=(\sigma_F^2+0.0002\cdot F^2)^{-1}$ converged at $R=0.042$ ($R_w=0.038$) [$R=0.072$ ($R_w=0.072$) for wrong absolute configuration], η refinement[10] gave $\eta=1.02(2)$. Further details may be obtained from the author E. E..

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