

Stereochemistry of organic compounds(29) : On the optical contribution and solvent effects of sugar xanthates

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Stereochemistry of Organic Compounds XXIX¹⁾

On the Optical Contribution and Solvent Effects of Sugar Xanthates

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In earlier studies²⁻⁷⁾, optical contributions of glucosides having xanthyl groups at C₁ and C₆ were reported. It was reported⁵⁾ that the optical contributions of C₁-xanthates of glucosides show clear differences between axial and equatorial configurations. These optical contributions are effective for determining the C₁-configuration of glucose. The report also shows that the first Cotton Effect of the C₆-xanthate of glucose is positive despite the differences of the C₁-configurations.

In the present study, optical contributions of glycosides having the different environment around C₅-Carbon are reported, since the optical activity of C₆-xanthate is due to the C₅-asymmetric center. For this purpose, the rotatory dispersion (RD), the circular dichroism (CD), and the ultraviolet absorption (UV) spectra will be measured using C₁-xanthates of xylose, glucose and glucuronic acid. In addition, this paper will report on those measurements of mannose C₁-xanthate which had not been made in an earlier study⁴⁾. The structure of the compounds studied are illustrated in **Figure 1**.

Furthermore, because the solvent effects are anticipated, these measurements were examined using ethanol as a polar solvent, and tetrahydrofuran (THF) and dioxane as non-polar solvents. Also, the proton nuclear magnetic resonance (¹H-NMR) spectra was measured in chloroform-*d*.

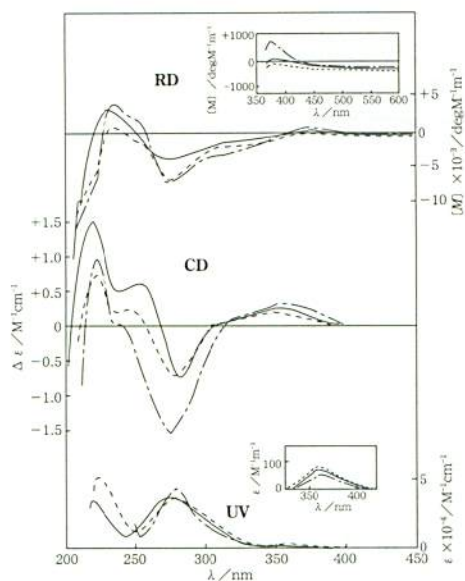


Figure 2. RD, CD and UV of I (— in ethanol, in THF, ---- in dioxane).

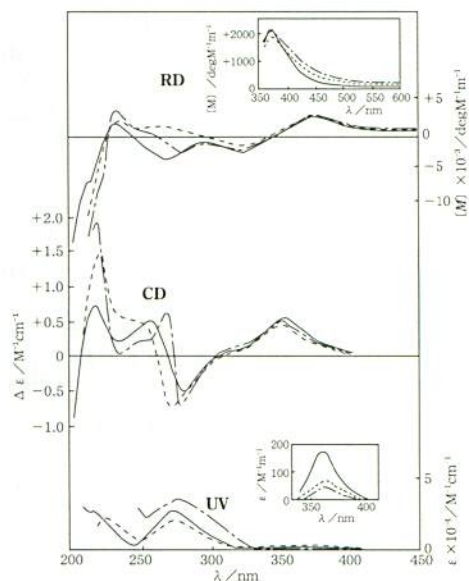


Figure 3. RD, CD and UV of II (— in ethanol, in THF, ---- in dioxane).

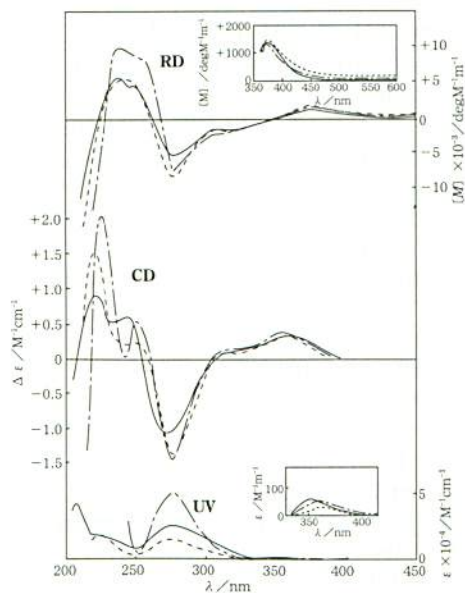


Figure 4. RD, CD and UV of III (— in ethanol, in THF, ---- in dioxane).

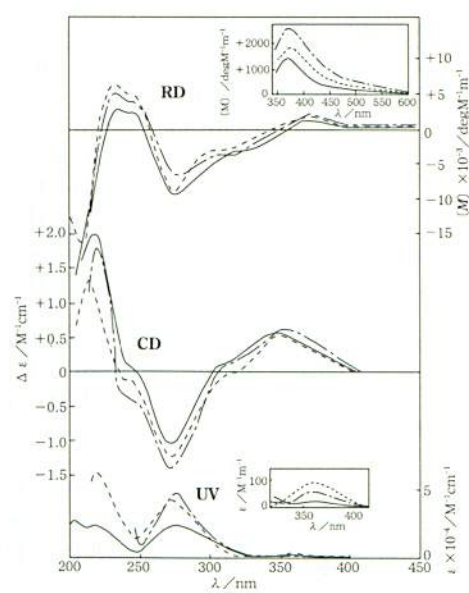


Figure 5. RD, CD and UV of IV (— in ethanol, in THF, ---- in dioxane).

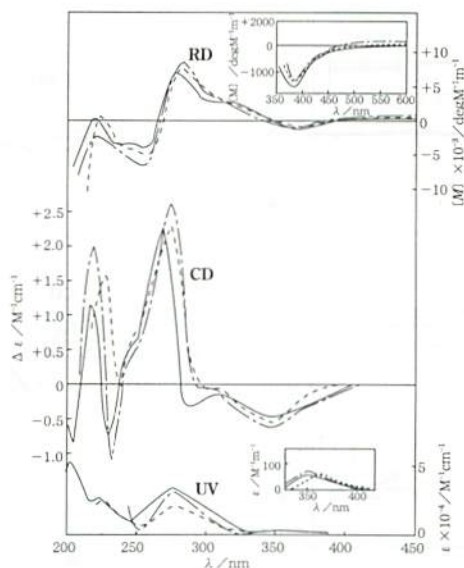


Figure 6. RD, CD and UV of V (— in ethanol, ---- in THF, -.- in dioxane).

Table 1. Data of CD, RD and UV spectra

Compound	spectrum	solvent	$\lambda_{\max}/\text{nm}(\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}; [\text{M}]/\text{deg M}^{-1}\text{m}^{-1}; \epsilon/\text{M}^{-1}\text{cm}^{-1})$
I	CD	ethanol	355(+0.241), 282(-0.761), 254(+0.609), 220(+1.52)
		THF* ¹	352(+0.199), 278(-0.721), 248(+0.249), 222(+0.748)
		dioxane	355(+0.314), 274(-1.55), 240(+0.0497), 222(+0.997)
	RD	ethanol	374(+4.19), 310(-2590, I* ²), 273(-3850), 231(+3260), 211(-10400)
		THF	372(-41.1), 332(-1850, I), 275(-6920), 256(-1560, I) 233(+823), 218(-7010, I)
		dioxane	375(+719), 318(-3160, I), 274(-7050), 254(-1400), 234(+4190)
	UV	ethanol	358(70.0), 274(37400), 218(32800)
		THF	358(80.1), 278(36500), 222(51000)
		dioxane	362(58.8), 278(42100)
II	CD	ethanol	354(+0.552), 283(-0.533), 260(+0.515), 218(+0.721)
		THF	353(+0.448), 274(-0.767), 222(+1.49)
		dioxane	352(+0.537), 280(-0.755), 269(+0.627), 220(+1.93)
	RD	ethanol	372(+2200), 323(-2620), 294(-1290), 270(-3660), 230(+1310), 212(-7180)
		THF	372(+2030), 325(-1970), 265(+1120), 247(+703), 232(+3590), 222(-7030, I)
		dioxane	371(+2240), 322(-2240), 290(-1730), 278(-2830), 258(+34.5), 234(+1930)

III	UV	ethanol	358(173), 272(29200), 216(27700), 208(30100)
		THF	360(68.3), 273(21400), 223(24600)
		dioxane	360(45.3), 276(36500)
	CD	ethanol	354(+0.330), 272(-1.10), 244(+0.612), 222(+0.930)
		THF	351(+0.315), 276(-1.37), 222(+1.53)
		dioxane	354(+0.385), 275(-1.45), 251(+0.542), 236(+2.02)
	RD	ethanol	373(+1310), 320(-1650), 304(-1570), 275(-5330), 250(+4770), 236(+5830)
		THF	373(+1510), 324(-1540), 308(-1420), 276(-8240), 250(+4620), 238(+5840)
		dioxane	371(+1410), 320(-2110), 306(-2100), 276(-7500), 255(-8770), 238(+10400)
IV	UV	ethanol	350(60.5), 276(27300), 218(19100), 205(42600)
		THF	360(34.1), 272(15400), 220(18500)
		dioxane	357(58.4), 274(49800)
	CD	ethanol	348(+0.548), 308(+0.066), 272(-1.07), 220(+2.08)
		THF	351(+0.533), 314(-0.077), 274(-1.28), 240(-0.153) 216(+1.33)
		dioxane	355(+0.610), 272(-1.43), 222(+1.81)
	RD	ethanol	370(+1450), 320(-3020,I), 276(-9410), 250(+2110), 230(+3130)
		THF	373(+1840), 316(-3160), 300(-3030), 276(-9200), 250(+4600,I), 233(+6750), 210(-16000)
		dioxane	373(+2320), 322(-3510), 306(-3530), 278(-6700), 254(+3500), 233(+5500)
V	UV	ethanol	360(12.5), 276(25000), 218(23800), 202(27200)
		THF	360(91.8), 275(42600), 220(61800)
		dioxane	359(52.2), 275(47800)
	CD	ethanol	350(-0.518), 310(-0.178), 287(-0.354), 268(+2.23), 228(-0.761), 216(+1.14), 204(-0.864)
		THF	349(-0.563), 308(-0.0794), 274(+2.30), 248(+0.742) 238(-0.0512), 226(+1.56)
		dioxane	347(-0.639), 275(+2.64), 231(-0.985), 219(+2.04)
	RD	ethanol	366(-1600), 322(+2430,I), 277(+6780), 256(-4140) 230(-3350), 218(+335)
		THF	368(-1270), 334(+1180,I), 282(+7410), 256(-5330), 236(-3890), 222(+759)
		dioxane	367(-1350), 302(+3650,I), 283(+8230), 256(-6730), 220(-2300)
UV	ethanol	350(57.3), 276(34800), 220(25400), 202(53400)	
	THF	352(57.3), 278(21400), 223(25100)	
	dioxane	350(67.4), 276(32500)	

*¹Tetrahydrofuran; *²Inflection point.

group on the axial and equatorial of C_2 respectively. Compound I shows negative rotation in RD in all solvents. The amplitudes of Cotton Effects in CD are affected by the different C_2 -configurations. This is shown by the weak Cotton Effect of Compound I as opposed to that Compound III. It is thus concluded that the rotational contribution to the RD of axial at C_2 is negative, and the Cotton Effect due to the C_1 -chromophore is weakened in magnitude, though equal in sign.

The CD and RD curves of Compounds II, III and IV in different solvents are shown in Figs. 8, 9 and 10 respectively. The configurations of C_1 , C_2 , C_3 , and C_4 , of those Compounds are identical. Therefore, a detailed comparison of the chiroptical data of those Compounds could lead to the optical contribution of C_5 of pyranose. In the cases of β - C_1 -xanthates, the optical contribution due to the band 1 around 350 nm are nearly equal, therefore, it is noted that chiroptical properties due to the band 1 are not affected by the different C_5 -environment. However, the optical contribution due to the band 2 around 275 nm is affected by the difference of C_5 -environment. The broad and blue-shifted negative Cotton Effects of Compounds III and IV around 270 nm are explained by a comparison with the Cotton Effects of Compound II. This is attributed to the absence of C_5 -asymmetric center in Compound II. In Compounds III and IV,

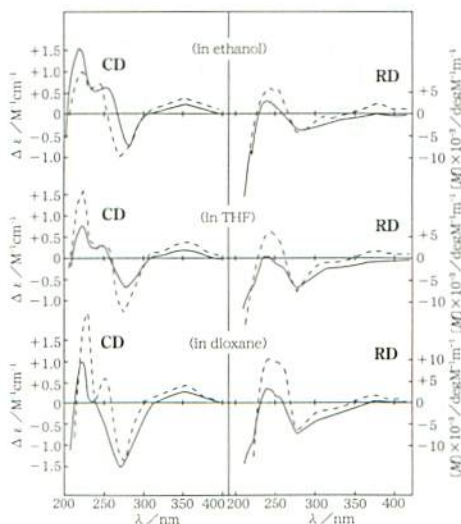


Figure 7. RD and CD of I and III in ethanol, THF and dioxane (— I, ---- III).

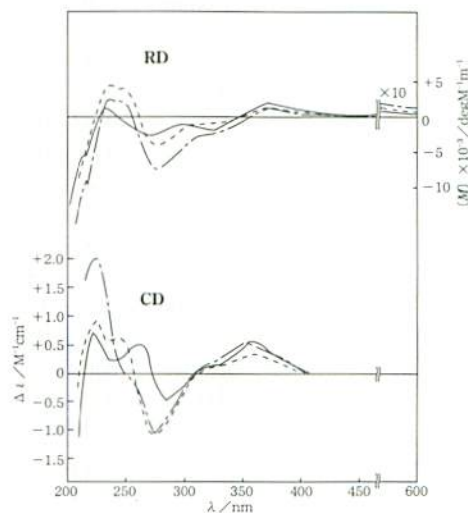


Figure 8. RD and CD of II, III and IV in ethanol (— II, ---- III, -.-IV).

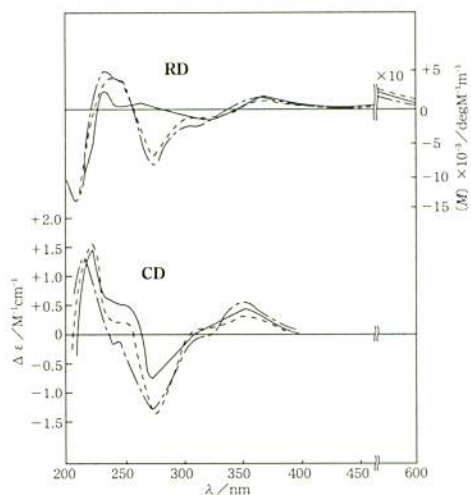


Figure 9. RD and CD of II, III and IV in THF (— II, III, --- IV).

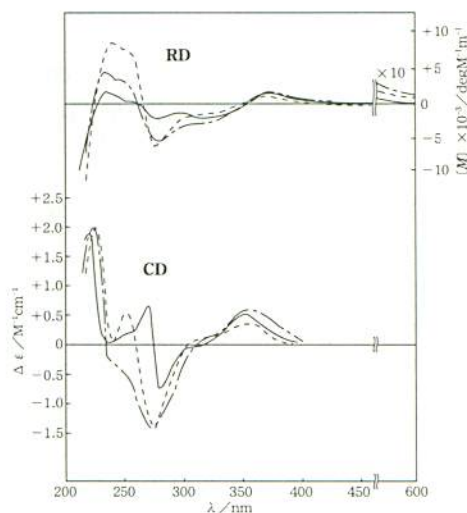


Figure 10. RD and CD of II, III and IV in dioxane (— II, III, --- IV).

negative Cotton Effects based on the band 2 centered at 272–274 nm are the same in site and strength, though the curvature of tails are slightly affected by the band 3 around 240–250 nm. The negative contribution to the CD around 240–250 nm by Compound IV is due to the C=O group directly attached at C₅.

In the previous study⁵⁾, the symmetry of CD curves of Compounds III and IV was explained by using the Newman projection. It is now noted that the CD and RD curves of Compound V are more symmetrical to Compound IV than to Compound III. The CD and RD curves of IV and V are illustrated in Figure 11, and the data of bands 1 and 2 are shown in Table 2 along with the UV data. As seen in Figure 11, the Compounds IV and V are symmetrical in each solvent. It is likely that the Compound IV is a mirror image of Compound V. As far as the band 1 of UV is concerned, the absorption maxima of Compound IV are shifted 8–10 nm to a longer wavelength region than Compound V. This bathochromic shift is thought to be attributed to the fact that the energy of Compound IV is lowered.

In order to investigate the conformation of Compounds IV and V, geometry optimizations were carried out using the MM2 (Molecular Mechanics 2) calculation on the CAChe System. The structures in Figure 12 represent the lowest energy conformations. It is clear that C₅-substituent of IV and C₁-substituent of V are symmetrical in

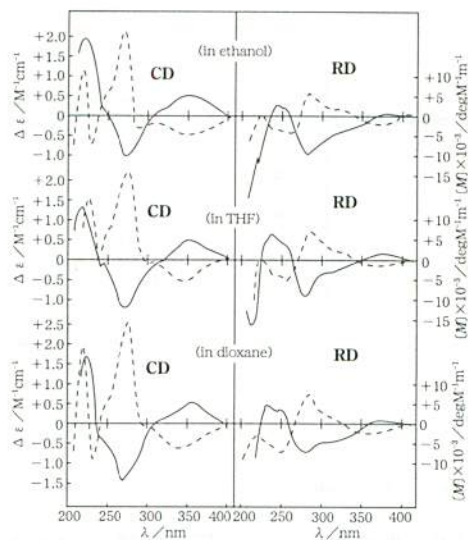


Figure 11. RD and CD of IV and V in ethanol, THF and dioxane (— IV, - - - V).

Table 2. Data of bands land 2 of Comps. IV and V

Solvent Comp.	CD		RD		$[\alpha]_{589}$	UV		
	Band1 $\Delta\epsilon$ (nm)	Band2 $\Delta\epsilon$ (nm)	Band1 [M] (nm)	Band2 [M] (nm)		Band1 ϵ (nm)	Band2 ϵ (nm)	
ethanol	IV	+0.548 (348)	-1.07 (272)	+1450 (370) P* ¹ -3020 (320) T	-9410 (276) T* ² +2110 (250) P	+11.9	12.5 (360)	25000 (276)
	V	-0.518 (350)	+2.23 (268)	-1600 (366) T +2430 (322) P	+6780 (277) P -4140 (256) T	+8.33	57.3 (350)	34800 (276)
THF	IV	+0.533 (351)	-1.28 (274)	+1840 (373) P -3160 (316) T	-9200 (276) T +4600 (250) P	+13.2	91.8 (360)	42600 (275)
	V	-0.563 (349)	+2.30 (274)	-1270 (368) T +1180 (334) P	+7410 (282) P -5330 (256) T	+22.4	57.3 (352)	21400 (278)
dioxane	IV	+0.610 (355)	-1.43 (272)	+2320 (373) P -3510 (322) T	-6700 (278) T +3500 (254) P	+16.7	52.2 (359)	47800 (275)
	V	-0.639 (347)	+2.64 (275)	-1350 (367) T +3650 (302) P	+8230 (283) P -6730 (256) T	+36.0	67.4 (350)	32500 (276)

*¹Peak,

*²Trough

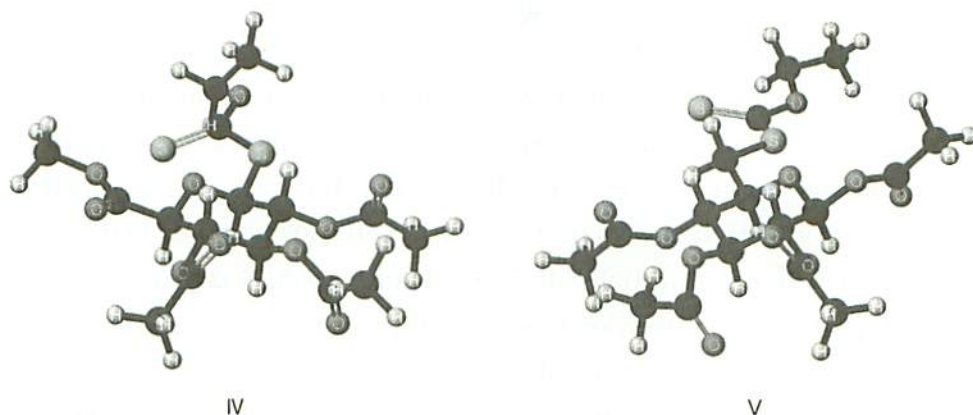


Figure 12. Optimized geometries of IV and V.

site, and the bulk of both substituents are the same because of the isomeric groups. Furthermore, in the case of V, the CH_2SCSOEt group as a whole behaves similar to a chromophore, since the SCS group attributes to the strong Cotton Effects.

The data presented in this paper leads to three conclusions. First, in the case of mannopyranosyl C_1 -xanthate, the rotational contribution of the RD of axial at C_2 is negative, and the Cotton Effect of the C_1 -chromophore is weakened. The second conclusion concerns the xylopyranosyl C_1 -xanthate. There, the first Cotton Effect is the same as that of hexoses having the same configurations at $\text{C}_1\sim\text{C}_4$, and over the second Cotton Effects are affected by the absence of C_5 -asymmetric center. In the final conclusion, the Cotton Effects of the SCS chromophore are governed by the asymmetric carbons adjacent to the ring oxygen in the pyranose ring.

Experimental

Measurements. The RD and CD were measured in ethanol, tetrahydrofuran and dioxane at 25°C , in the wavelength region from 200 to 600 nm with JASCO/UV-5 type optical rotatory dispersion recorder. The UV spectra were measured with the same conditions as the RD and CD measurements by Hitachi Model 320 Spectrophotometer. The $^1\text{H-NMR}$ spectra were measured on a Hitachi Model R-24B at room temperature in $\text{DMSO}-d_6$ as a solvent. Chemical shifts are in ppm (δ) from SiMe_4 as

the internal standard and J -values are given in Hz. The geometries of Compounds IV and V were optimized using MM2 calculations on CAChe System (Sony Tektronix).

Materials. The samples were prepared according to the methods of literature⁹⁻¹².

2,3,4,6-Tetra-O-acetyl- β -D-mannopyranosyl 1-Ethylxanthate (Compound I)⁹. Colorless crystals, mp 127-128°C; ¹H-NMR δ =1.43 (3 H, t, J =7.2 Hz), 1.99 (3 H, s), 2.07 (3 H, s), 2.08 (3 H, s), 2.18 (3 H, s), 3.60-4.10 (1 H, m), 4.12-4.32 (2 H, d, J =5.4 Hz), 4.66 (2 H, q, J =7.2 Hz), 5.15-5.38 (2 H, m), 5.58-5.79 (2 H, m).

2,3,4,6-Tri-O-acetyl- β -D-xylopyranosyl 1-Ethylxanthate (Compound II)¹⁰. Colorless needles, mp 105-105.5°C; ¹H-NMR δ =1.43 (3 H, t, J =7.1 Hz), 2.06 (9 H, s), 3.56 (1 H, dd, J =12.0 and 7.2 Hz), 4.22 (1 H, dd, J =12.0 and 5.4 Hz), 4.66 (2 H, q, J =7.2 Hz), 4.99-5.29 (3 H, m), 5.67 (1 H, d, J =7.2 Hz).

2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosyl 1-Ethylxanthate (Compound III)⁹. Colorless needles, mp 75-76°C; ¹H-NMR δ =1.44 (3 H, t, J =7.2 Hz), 2.02 (9 H, s), 2.07 (3 H, s), 3.60-4.10 (1 H, m), 4.21 (2 H, d, J =4.2 Hz), 4.66 (2 H, q, J =7.2 Hz), 5.00-5.61 (4 H, m).

Methyl 2,3,4-Tri-O-acetyl- β -D-glucopyranuronate 1-Ethylxanthate (Compound IV)¹¹. Colorless needles, mp 114-115°C; ¹H-NMR δ =1.42 (3 H, t, J =7.2 Hz), 2.01 (9 H, s), 3.74 (3 H, s), 4.07-4.27 (1 H, m), 4.65 (2 H, q, J =7.2 Hz), 4.97-5.70 (4 H, m).

6-Desoxy-6-ethylxanthogen- β -D-glucopyranose Tetraacetate (Compound V)¹². Colorless needles, mp 121-123°C; ¹H-NMR δ =1.41 (3 H, t, J =7.2 Hz), 2.00 (6 H, s), 2.09 (6 H, s), 3.16 (1 H, dd, J =14.4 and 7.2 Hz), 3.48-4.05 (2 H, q, J =7.2 Hz), 4.93-5.46 (3 H, m), 5.70 (1 H, d, J =8.4 Hz).

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