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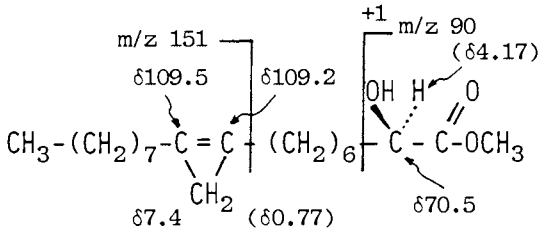
Stereochemistry of Methyl 2-Hydroxysterculate from *Hibiscus rosa-sinensis*

Munehiro NAKATANI* and Tsunao HASE
Department of Chemistry, Faculty of Science, Kagoshima University,
1-21-35 Korimoto, Kagoshima 890

The absolute configuration of the asymmetric carbon (C-2) of methyl 2-hydroxysterculate was determined as *R* by applying the dibenzoate chirality method.

2-Hydroxysterculic acid was first isolated from alkaline hydrolysis products of glycerides from *Pachira* and *Bombacopsis* oil, and the stereochemistry at C-2 was inferred as *R* from the specific rotation ($[\alpha]_D$ -5.1°) of the methyl ester **1** by analogy with some α-hydroxyacid methyl esters.[1] We have unambiguously confirmed it from the CD spectrum of a 1,2-dibenzoate derivative **4** by applying a dibenzoate chirality method of Harada and Nakanishi.[2]

Compound **1** ($C_{20}H_{36}O_3$; $[\alpha]_D$ -10°), 2.8 mg, was isolated from the root bark (1.5 kg) of *Hibiscus rosa-sinensis*[3] and identified as methyl 2-hydroxysterculate by spectrometry.



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To determine the absolute configuration of the asymmetric carbon (C-2), we applied the dibenzoate chirality method to a dibenzoate **4** derived from **1** as follows. The cyclopropene ester **1** was hydrogenated over Pd catalyst to give a saturated ester **2**, which was in turn reduced with $LiAlH_4$ to give a 1,2-diol **3**. The 1,2-dibenzoate **4** was prepared by acylation of **3** with benzoyl chloride in pyridine with a catalytic amount of 4-dimethylaminopyridine.

The ^1H NMR spectrum (in $CDCl_3$) of the dibenzoate **4** showed two geminal protons due to the benzoyloxymethylene group at δ 4.48(dd, J= 11.7 and 6.8 Hz) and 4.57(dd, J= 11.7 and 3.4 Hz). The proton at higher field and with larger vicinal coupling constant was assigned to the H_1-Pro-*S* in 2*R*.[4] The

assignment of the two prochiral protons at C_1 and an application of the Karplus type equation proposed by Haasnoot et al.,[5,6] revealed that **4** existed predominantly in a *gt* conformer in the solution (see Fig. 1) and its population was 58% in $CDCl_3$ and 62% in MeOH.

The CD spectrum (Fig. 2) of **4** gave a negative exciton coupled CD having the first band at 237 nm with a negative sign and the second band at 224 nm with a positive one. The CD peaks can be attributed to the interaction between the di-O-benzoyl chromophores at C_1 and C_2, and the negative sign of the Cotton effect indicates that C_1-O and C_2-O bonds adopt a negative helicity, namely, *gt* conformation in 2*R* and *gg* in 2*S* (Fig. 1): there exist three kinds of staggered conformations in each case of 2*R* and 2*S*, namely, *gg*, *gt*, and *tg* about C_1-C_2 axis. In the case of 2*R*, conformer *gt* of the C_1-C_2 bond should have a negative contribution, while conformer *gg* should have a positive contribution to the exciton coupling. On the other hand, the reverse contributions should be predictable in the case of 2*S*. Here, the contribution of conformers *tg* with the anti-periplanar disposition of the two benzoate will be negligible.

The results of the conformational analysis by NMR spectroscopy and the CD studies elucidated that the absolute configuration of the C-2 should be *R*.

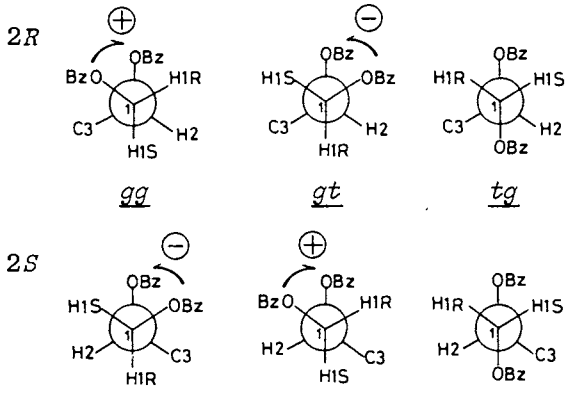

Fig.1. Three possible conformers, *gg*, *gt*, and *tg* in each 2*R* and 2*S*, about the C_1-C_2 bond.

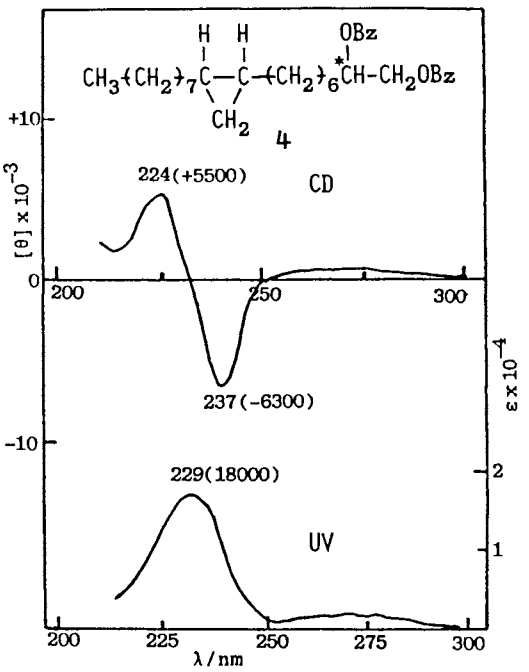

Fig.2. CD and UV spectra of 4 in MeOH.

References
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