to be expected by the ferrocene force field deviate grossly from the experimental values. This is in marked contrast to a similar study of a series of benzene sandwich compounds.[2] These calculations, which used the $Cr(C_6H_6)_2$ force field, reproduced very well the qualitative appearance of the pattern of such framework vibrations in different compounds.

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Investigation of Lactonic Acids in the Latex of *Euphorbium canariensis* L. Isolation of D-Glucaric Acid

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During the investigation of acids from succulent plants [1-3] it became evident that acids capable of forming lactones, often occur within this plant group. Evidence will here be advanced for the presence of D-glucaric acid in the latex of *Euphorbium canariensis* L. Aldaric acids have seldom been found in the free state in plants. However, D-glucaric acid has been found previously in the latex of *Ficus elastica* Roxb.[4] and in *Phaseolus aureus* seedlings.[5]

Experimental. Latex of *Euphorbium canariensis* was repeatedly extracted with water (90°C). Calcium hydroxide solution was added to the eluates until pH 6.5 was obtained, followed by extraction with ether. On concentration of the aqueous solution a calcium salt precipitated (yield 4 %). Titration of the calcium salt with perchloric acid: Found: E = 125.2. (Calc. for $C_6H_8O_8Ca$: 124.11.) The salt was deionized with Dowex 50 (H^+) and furnished a syrup. Cryoscopic measurements gave a molecular weight of about 211. (Calc. for $C_6H_{10}O_8$: 210.14.) Back-titration after dissolution in sodium hydroxide at room temperature: Found: E = 104.5. (Calc. for $C_6H_{10}O_8$: 105.07.) The acid was dried over phosphorus pentoxide at 0.02 mm Hg at 25°C overnight and gave a mixture, presumably consisting of D-glucaric acid, the two monolactones and the two dilactones.[6] $[\alpha]_D^{20} = +93° \rightarrow +45°$ after 24 h (c = 1.5; water). IR-spectrum identical with that of the authentic substance. The mixture was subsequently dried over phosphorus pentoxide at 0.01 mm Hg at 100°C until constant weight was obtained. (Found: C 41.41; H 3.60. Calc. for the dilactone $C_6H_6O_6$: C 41.39; H 3.45.) Dibenzylamide, m.p. 201–202°C, undepressed in mixture with an authentic sample. (Found: C 61.88; H 6.19; N 7.22. Calc. for $C_{20}H_{24}O_6N_2$: C 61.84; H 6.23; N 7.21.)

Paper chromatography. Paper chromatograms were run on Whatman No. 1 in the following solvent systems (v/v): A. Ethyl acetate, pyridine, water, 8:2:1. B. Ethyl acetate, acetic acid, formic acid, water, 18:3:1:4. C. Ethyl acetate, pyridine, acetic acid, water, 5:5:1:3. D. Ethyl methyl ketone, acetic acid, water, saturated with boric acid, 9:1:1.

Substances were located on chromatograms with the following reagents: a. Bromophenol Blue, 0.05 %, in water. b. Hydroxylamine-ferric chloride.[7] c. Periodic acid-benzidine.[8] d. Silver nitrate-sodium hydroxide.[9] Chromatographic mobility of the acid in the solvent systems B and C was identical to that of the reference compound. The acid could be detected by either of the reagents quoted. The chromatographic mobility of the benzylamide in solvent system B was indistinguishable from that of the reference substance. The benzylamide was detected by reagent d.

Esterification with methanol and Dowex 50 (H^+). Esterification was effected by refluxing the acid (50 mg) with methanol and Dowex 50 (H^+) for 24 h. This treatment resulted in the conversion of the acid into its dimethyl ester and other reaction products, possibly the methyl ester monolactones and the dilactones (totally 56 mg). The chromatographic mobilities of the methyl esters and the dilactones

were identical to those of the reference compounds. The methyl esters were detected by reagents b, c, and d, the dilactones by reagent d.

Reduction. An aliquot of the esterification product (20 mg) was reduced with lithium aluminium hydride (0.3 g) in tetrahydrofuran (30 ml) by gentle reflux for 2 h. The reaction product (13 mg) furnished an alcohol, indistinguishable from D-glucitol by chromatographic investigation in the solvent systems A, B, and D. The alcohol was detected by reagent c.

De-O-methylation [10] failed to cause a change in chromatographic mobility of the alcohol.

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N-Quarternary Compounds

Part XX.[1] Stereochemical Studies

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Our stereochemical studies [2,3] in the dihydrothiazolo[3,2-a]pyridinium-8-oxide series required the establishment of relative configuration by X-ray analysis. For this purpose we have synthesized a bromosulphoxide (VI).

The product obtained by the addition of the thiolactam (I) to α-bromoisocrotonic acid followed by cyclisation of the adduct over the annular nitrogen has been assigned a *trans* configuration on the basis of the value of the coupling constant, $J_{2,3} < 1$, in the NMR spectrum in TFA.[2] The *trans* configuration has now been confirmed by X-ray analysis of VI.[4]

Peracid oxidation of the thioether (III) gave the diastereomeric sulphoxides in the ratio 9:1. The stereoselectivity in the oxidation was further increased by having a *trans* methyl group in the 2-position (IV). In agreement with NMR arguments [3] *cis* oxidation of the sulphur with respect to the carboxy group was assumed. For this assumption to be correct the carboxy group must participate in the oxidation. The mechanism proposed is either a rapid, preferential oxidation of the carboxy group, the formation of a diacylperoxide intermediate, or the formation of a hydrogen bonded complex between the peracid and the carboxy group. The actual species involved should depend on the experimental conditions. X-Ray analysis of VI confirms that the sulphinyl oxygen is *cis* with respect to the carboxy group.[4]

The sulphoxides are very readily decarboxylated. We have used this in the preparation of optically active sulphoxides of type VIII. Thus oxidation of compound III with the L-configuration followed by decarboxylation led to an optically active sulphoxide assigned the absolute *S*-configuration.[3] From the discussion above it follows that this assignment is in agreement with the relative stereochemistry of VI determined by X-ray analysis.[4]

The sulphoxide (VI) is formulated as a phenolate rather than as a carboxylate since the X-ray analysis [4] shows strong