the solvent, the residue was subjected to preparative TLC in ether/light petroleum (1:5) affording 103 mg of (−)-Δ^6-THC (*9*), ^{14}C-labelled in the aromatic ring. The compound had identical IR-spectrum, TLC- and GLC-behaviour as an authentic sample. Specific activity 0.31 μC/mg.

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The Basicities of Alkyl-1,3-dioxolanes and Their Implications to Hydrolytic Decomposition

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In previous studies [1,2] marked differences were found in the rates of hydrolysis of alkyl-1,3-dioxolanes and acyclic acetals. First, most of the acetone derivatives of 1,3-dioxolane hydrolyzed only one power of ten faster than the corresponding acetaldehyde derivatives although a rate increase by a factor of $10^{3.5}$ was expected due to the inductive polar effects. In the case of the fully methyl-substituted acetone derivative the rate was lower than that of the acetaldehyde derivative. Second, the rate differences between the isomeric compounds could not be explained to be consequences of initial state energy differences because the isomers of higher stability usually hydrolyzed more rapidly than the less stable forms. Third, the rate coefficients decreased with increasing number of 4- and 5-methyl substituents. These results were most reasonably explained by steric interactions.[1,2] As a consequence of the formation of a partial double bond in the attainment of the transition state of the hydrolysis, the bonds attached to the atoms of this double bond tend to become coplanar. Thus one of the substituents in position 2 must bend toward the average plane of the ring. It is obvious that this kind of change cannot take place without steric strain. Because steric effects are marked in the hydrolysis of most alkyl-1,3-dioxolanes, it is impossible to obtain information about other factors influencing the hydrolysis by comparing rate coefficients only. The basicities of various alkyl-1,3-dioxolanes were measured in this work to dissect the overall rates into partial factors, namely, the protonation pre-equilibrium constant and the rate coefficient of the rate-determining heterolysis.

Experimental. The samples of 1,3-dioxolanes used in the determinations of basicities were those that had been prepared for previous kinetic measurements.[1,2] The physical constants of the compounds were described in that

Table 1. O—D band shifts of methanol-d_1 in alkyl-1,3-dioxolanes and the pK_a values of these acetals in water at 25°C.

1,3-Dioxolane	O—D band position (cm^{-1})	O—D band shift (cm^{-1})	pK_a
1,3-Dioxolane	2599.8	90.1	−3.8
4,5-Dimethyl- (*trans*)	2605.7	84.2	−4.3
4,5-Dimethyl- (*cis*)	2608.0	81.9	−4.5
4,4,5-Trimethyl-	2597.5	92.4	−3.6
4,4,5,5-Tetramethyl-	2608.0	81.9	−4.5
2,4-Dimethyl- (*trans*)	2602.7	87.2	−4.0
2,4,5-Trimethyl- (*cis,cis,trans*)	2603.8	86.1	−4.1
2,4,5-Trimethyl- (*cis*)	2604.6	85.3	−4.2
2,4,4,5,5-Pentamethyl-	2603.3	86.6	−4.1
2,2-Dimethyl-	2609.4	80.5	−4.6
2,2,4,4-Tetramethyl-	2607.6	82.3	−4.4
2,2,4,5-Tetramethyl- (*trans*)	2609.6	80.3	−4.6
2,2,4,5-Tetramethyl- (*cis*)	2605.2	84.7	−4.2
2,2,4,4,5-Pentamethyl-	2605.6	84.3	−4.3
2,2,4,4,5,5-Hexamethyl-	2600.0	89.9	−3.8
4-Chloromethyl-	2618.1	71.8	−5.2
2-Methyl-4-chloromethyl- (*cis*)	2616.5	73.4	−5.1
2-Methyl-4-chloromethyl- (*trans*)	2609.8	80.1	−4.6
2,2-Dimethyl-4-chloromethyl-	2615.2	74.7	−5.0
2-Ethyl-4-methyl- (*trans*)	2600.5	89.4	−3.9
2-Propyl-4-methyl- (*cis*)	2602.1	87.8	−4.0
2-Propyl-4-methyl- (*trans*)	2602.0	87.9	−4.0
2-Methyl-2-ethyl-	2608.2	81.7	−4.5
2,4-Dimethyl-2-isopropyl-	2605.1	84.8	−4.2

context. Gas chromatographic analyses revealed that the proportion of impurities was less than 1 % in all samples.

The practical performance of the IR measurements has been described earlier.[3] About ten determinations were carried out on each of the studied compounds.

The O—D band positions of methanol-d_1 in various 1,3-dioxolanes at 25°C are collected in Table 1. The basicities of the studied 1,3-dioxolanes in water were calculated from the measured O—D band shifts ($\Delta\nu$) using eqn. (1) experimentally

$$pK_a = 0.0789\Delta\nu - 10.91 \qquad (1)$$

determined for ether-type compounds in a previous work.[3] The calculated pK_a values are given in the last column of Table 1.

When the effect of the aldehyde component on the basicity of the oxygen atoms of 1,3-dioxolanes is studied, only a slight variation in the pK_a values is found in the series of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, acetone, and methyl ethyl ketone derivatives. The same applies also to the series of 1,3-dioxolanes derived from different alcohols. An increase in basicity would be expected with the increasing number of 4- and 5-methyl groups because it was previously found that a linear correlation exists between the basicity of the oxygen atom and the electropositivity of the alkyl group attached to the oxygen atom in acyclic acetals.[3] This kind of change is not, however, found in the studied methyl-1,3-dioxolanes. The effect of highly electronegative substituents in the alcohol component was also studied. In the case of chloromethyl-substituted derivatives, the basicity is lower than in the corresponding

methyl-substituted derivatives but the substituent effect is much smaller than in the corresponding acyclic acetals. Thus we can conclude that the protonation of the oxygen atoms is less sensitive to inductive polar effects of the substituents in 1,3-dioxolanes than in the acyclic acetals.

The overall rate coefficient $k_{H_3O^+}$ for the hydrolysis of a 1,3-dioxolane by the A-1 mechanism of acetals (2) can be expressed by eqn. (3), where k_2 is the rate coefficient

$$S + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ \xrightarrow{k_2} \text{products} \qquad (k_2 \ll k_{-1}) \qquad (2)$$

$$k_{H_3O^+} = k_2/K_a \qquad (3)$$

of the rate-determining heterolysis and K_a the equilibrium constant for the protonation pre-equilibrium. Because only small differences in the equilibrium constants K_a are found in alkyl-1,3-dioxolanes, the differences in the observed rate coefficients are mainly due to the partial reactions in which the 1,3-dioxolane ring is cleaved. This observation confirms the previous conclusions that the relatively low rates of the hydrolysis of a number of 1,3-dioxolanes is due to low rates of ring cleavage and that the retardation must be steric in character.

The rate coefficients k_2 can be evaluated from the experimental data using eqn. (3). As recorded above, the values of K_a are of the order of 10^4 M for most of the studied 1,3-dioxolanes. Using the second-order rate coefficients measured in a previous work,[2] the following rate coefficients are obtained for the heterolysis reactions: $10^{-2} - 10^{-3}$ s^{-1} for the 1,3-dioxolanes derived from formaldehyde, $10 - 10^2$ s^{-1} for the acetaldehyde derivatives, and $1 - 10^3$ s^{-1} for the acetone derivatives. When these rate coefficients are compared with the estimated maximum value, $10^6 - 10^8$ s^{-1},[4] for the rate coefficient k_{-1} of a proton transfer from the protonated acetal to water, it is found that also in the case of acetone derivatives, in which the heterolysis is greatly accelerated owing to the high stability of the intermediate ion, k_2 is much smaller than k_{-1}. Thus additional and independent evidence has been obtained for the A-1 hydrolysis of 5-membered cyclic acetals.

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Synthesis of Sambubiose

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Sambubiose, 2-*O*-β-D-xylopyranosyl-D-glucose, was prepared by condensation of benzyl 3,5,6-tri-*O*-benzyl-α-D-glucofuranoside and 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide followed by removal of blocking groups.

The disaccharide moiety of a cyanidine glycoside isolated from *Sambucus nigra* was first believed to be primverose, 6-*O*-β-D-xylopyranosyl-D-glucose, but was later shown to be 2-*O*-β-D-xylopyranosyl-D-glucose, and was given the name sambubiose.[1] It is an uncommon constituent of flavanoids,[2] and has never been isolated as a free sugar. In the present communication, the synthesis of sambubiose is reported.

Benzyl 3,5,6-tri-*O*-benzyl-α-D-glucofuranoside was prepared from 1,2-*O*-isopropylidene-D-glucofuranose and purified *via* its crystalline acetate.[3] It was then condensed with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide, using mercuric cyanide-mercuric bromide in acetonitrile, as devised by Helferich.[4] The condensation product was isolated by column chromatography on silicic acid, deacetylated and, after a further chromatographic purification, debenzylated by catalytic hydrogenation. Crystallisation of the resulting syrup from ethanol yielded sambubiose, m.p. 202–203°. The optical rotation of the disaccharide, in water, decreased from $[\alpha]_{578}$ +32° (5 min) to +17° (48 h), demonstrating that it had crystallised as the α-form.