However, it should be stressed, that the reactivities of the arabinoglucuronoxylan and the model substances are not strictly comparable, for the reactivity of the furanosidic residues is undoubtedly influenced by its position in the polysaccharide molecule.

Experimental. All melting points are corrected. Distillations were carried out under reduced pressure. Paper chromatography was conducted on Whatman No. 1 filter paper using the following solvent systems:

A. Butanol-pyridine-water, 6 : 2 : 3

B. Butanone, saturated with water.

Substances. The D-xylo- and D-galacto-furanosides were prepared according to Augestad and Berner.[4] Methyl-α-D-mannofuranoside was prepared according to Haworth *et al*[6]. Methyl-α-L-arabinofuranoside was prepared as described for the corresponding D-form by Wright and Khorana[5]. It had m.p. 45—48° and $[\alpha]_D^{20}$ — 124°(water) in good agreement with reported values.

Methyl-β-D-glucofuranoside was prepared by a Fisher synthesis, following the technique devised by Augestad and Berner[4]. Glucose (60 g) was dissolved by stirring in 0.55 % methanolic hydrogen chloride; the solution was kept at room temperature overnight. The acid was removed by treatment with lead carbonate and the solution concentrated to a syrup. Paper chromatographic analysis of this syrup in solvent system B revealed the presence of four components: glucose; a mixture of α- and β-pyranosides, migrating as a single component; and the α- and β-furanosides, which were well separated. Part of the syrup (37 g) was added to the top of a cellulose column (6.4 × 130 cm) which was then eluted with solvent system B. Methyl β-D-glucofuranoside, the faster of the two anomers, was eluted between 18 000—30 000 ml. Concentration of this fraction gave methyl β-D-glucofuranoside as a chromatographically-pure syrup showing $[\alpha]_D^{20}$ —54° in water. Comparison with the reported value $[\alpha]_D$ —77°) indicated that the substance was incompletely dried.

Reaction of the glycosides with alkali was carried out as previously described[2]. In the case of the uronides, the following procedure was employed. After alkaline hydrolysis the reaction mixture was neutralised with hydrochloric acid and concentrated to dryness. The residue was dissolved in water and an aliquot concentrated and subjected to methoxyl analysis.

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Confirmation of the Structure of Ketomanoyl Oxide

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Recent work in this laboratory has shown that hinokiol, hinokione [1] and totarolone [2] all have an oxygen function at C(3) (steroid numbering). The original assignment [3] of the keto group of ketomanoyl oxide to the 2-position has recently been questioned [4] *.

In connection with mass-spectrometric work on related substances [5] the mass-spectra of the tetra-deuterated and non-deuterated dihydroketomanoyl oxide were recorded (Figs. 1 and 2). A comparison of the two spectra shows clearly that 4 hydrogen atoms have been replaced by deuterium, since the peaks at m/e 307 ($M + 1$), 291 (M-15), and 277 (M-29) in the spectrum of dihydroketomanoyl oxide (Fig. 2) are found 4 mass units higher, at m/e 311, 295, and 281, in the spectrum of deuterated dihydroketomanoyl oxide (Fig. 1). These peaks are probably due to ions obtained from the molecule after addition of a proton (307 and 311), removal of a methyl group (291 and 295) and an ethyl group (277 and 281), respectively. The result shows that position 2, originally assigned to the oxo

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* During the preparation of this manuscript a communication has appeared in which the same approach led to similar results. Grant, P.K. and Hodges, R. *Chem. & Ind. London* **1960** 1300.
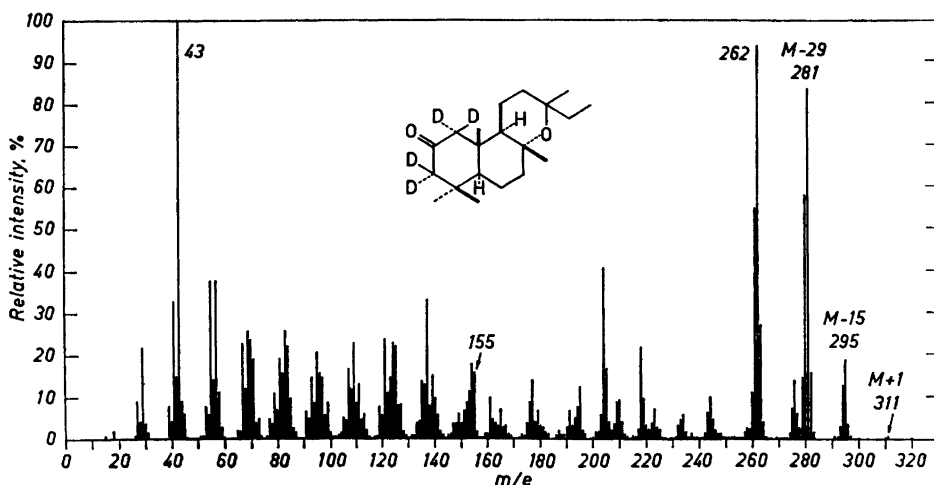
Fig. 1. Mass-spectrum of tetradeuterodihydroketomanoyl oxide.

group, is the only possible position for this group in ketomanoyl oxide.

The peak at *m/e* 151 in the spectrum of dihydroketomanoyl oxide, which occurs at *m/e* 155 in the spectrum of deuterated dihydroketomanoyl oxide, most probably is due to an ion originating from ring *A* by rupture of the C(6)—C(7) and C(9)—C(10) bonds and removal of a proton. Corres-

ponding peaks have been observed in spectra of compounds with the same configuration as in ketomanoyl oxide at C(5), C(9), and C(10), *e.g.* torulosol, dihydrotorulosol, torulosal, manool, dihydromanool, manoyl oxide, agathadienecarbinolcarboxylic acid [5], methyl cryptopimarate and methyl pimarate [6] (dextropimarate) and are more fully discussed elsewhere [5].
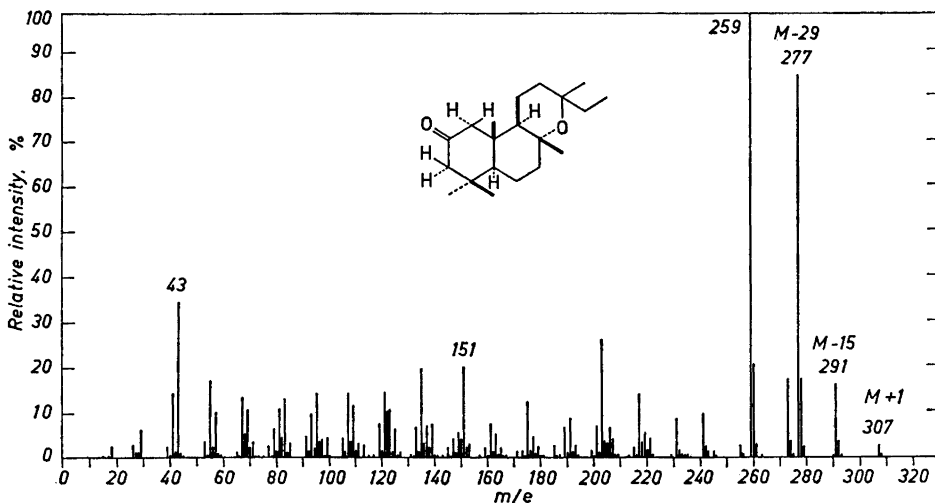

Fig. 2. Mass-spectrum of dihydroketomanoyl oxide.

Examination of the PMR-spectrum of dihydroketomanoyl oxide confirms the mass-spectrometric results. The intensity of the signal at 206 c/s (from internal benzene standard in dilute CCl_4 solution; 40 Mc/s) indicates the presence of four hydrogen atoms on the carbon atoms adjacent to the keto group.

Ketomanoyl oxide, in methanol solution, showed a comparatively [7,8] large positive Cotton effect ($[a]_{500} + 400°$; $[a]_{313} + 3 300°$; $[a]_{276} - 3 700°$; $[a]_{278} - 3 600°$), which, as in the case of 3-oxo terpenoid-type compounds, was not lowered on addition of hydrochloric acid [9]. The inability to form a hemiketal is probably caused by 1,3-interaction of the axial methyl substituents.

Deuterium exchange [10] was effected by boiling dihydroketomanoyl oxide [4], m.p. $91 - 92°$ (50 mg), with a solution obtained from sodium (7 mg), O-deuteromethanol (1.5 ml) and deuterium oxide (0.5 ml) under oxygen-free nitrogen for 10 min. followed by removal of the solvents. The proceedure was repeated three times with fresh solvents. Addition of deuterium oxide (3 ml) to the residue and extraction with dry ether gave, after drying, removal of the solvent and sublimation of the residue, tetradeuterodihydroketomanoyl oxide, m.p. $89 - 92°$.

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Inductive Effects on the Donor Strengths of Some Oxo Compounds

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In a recent paper [1] it was reported that esters and ketones have almost equal donor strengths in reactions with $SbCl_5$. Passing from ketones to esters two main effects can be predicted. Thus the inductive effect would lead to a reduction of the donor strength owing to withdrawal of electrons from the carbonyl oxygen atom. This would be opposed, however, by delocalization of one of the lone pair of electrons of the ether oxygen atom. For the carbonyl oxygen atom the two effects seem to be of the same magnitude and on balance no appreciable difference is obtained. This is also reflected in the $C=O$ bond lengths, which are almost equal in ketones and esters. On the other hand, in the presence of halogens, the inductive effect is dominant and the $C=O$ bond lengths are shorter [2]. It has been shown moreover that halogen substitution has the same effect on the donor strengths of compounds containing $S=O$, $Se=O$ and $P=O$ bonds [1]. In this paper we report the effect of alkoxy substitution on the donor strengths of these compounds in order to determine the balance between the inductive and delocalization effects. The following esters have been studied: $(CH_3O)_2SeO$, $(CH_3O)_2SO$, $(CH_3O)(CH_3)SO_2$ and $(CH_3O)_3PO$.

Experimental. Dimethylselenite, $(CH_3O)_2SeO$, was prepared according to Michaelis and Landmann [3]. B.p. $+ 62 - 65°/11$ mm.

Dimethyl sulfite, $(CH_3O)_2SO$, was prepared according to Woss [4]. B.p. $+ 125°$.