why phosphorus is not detected in the powder photograph may be the low diffracting power of phosphorus in combination with the small amount present as much of it condenses on cooler parts of the silica tubes.

The symmetry and approximate cell parameters were derived from oscillation and Weissenberg photographs obtained by rotating the crystal around an axis which proved to be the twofold axis of a monoclinic unit cell. The cell dimensions were refined by the method of least squares using a program written by J. Tegenfeldt at this institute. The observed $\sin^2\theta$ values used in the refinement are given in Table 1. They were obtained from a powder photograph of the sample containing 60 at. % phosphorus. The dimensions of the monoclinic unit cell so obtained are:

$$a = 5.8651 \pm 0.0005 \text{ Å}$$
$$b = 14.435 \pm 0.001 \text{ Å}$$
$$c = 4.6712 \pm 0.0004 \text{ Å}$$
$$\beta = 108.399 \pm 0.007°$$
$$V = 375.27 \text{ Å}^3$$

The errors given are standard deviations.

As can be seen in Table 1 the indices for the observed reflexions fulfill the condition $h+k=2n$ indicating a C-centered unit cell. This condition was also verified from Weissenberg photographs of three different layer lines. As no restrictions were found for the occurrence of $h0l$ reflexions possible space groups are $C2/m$, Cm, and $C2$, probably with eight gold atoms in each unit cell. It can also be mentioned that the oscillation photographs showed a tendency for the layer lines with k odd to be markedly weaker than the layer lines with k even.

The X-ray data given here are probably for the phase previously denoted Au_2P_3, although a correct assignment of the true stoichiometry will have to await a complete structure determination.

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Flavonoids of *Lotus* L.

II.* Synthesis of the Flavonols Corniculatusin and Patuletin

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In a previous paper,[1] the isolation and constitutional elucidation of a new flavonol glycoside, corniculatusin-3-galactoside, from the flowers of *Lotus corniculatus* L. have been described. The constitution 5,7,3′,4′-tetrahydroxy-8-methoxy-flavonol-3-*O*-β-D-galactoside (Ia) was proposed for the flavonoid, mainly based on spectroscopic evidence. The constitution 5,7,3′,4′-tetrahydroxy-6-methoxy-flavonol-3-*O*-β-D-galactoside was excluded on the basis of the chemical shift of the A-ring proton in the selectively detrimethylsilylated pertrimethylsilyl ether of the aglycone and the deviation in the melting points of the permethylated derivatives of the aglycone and patuletin.

The synthesis of 5,7,3′,4′-tetrahydroxy-8-methoxy-flavonol (Ib) and 5,7,3′,4′-tetrahydroxy-6-methoxy-flavonol (Ic), as described in this paper, and comparison of their data with those of the natural aglycone, confirmed the constitution (Ia) of the glycoside.

Many authors have described condensations of unsymmetrically substituted 2,6-dihydroxy-ω-methoxy-acetophenones with benzoic anhydrides, under Allan-Robinson-Kuhn conditions, leading to isomeric 6- and 8-substituted 3-methoxy-flavones (see, *e.g.*, Ref. 2). Using the same method, but replacing the ω-methoxy moiety by a ω-benzoyloxy group, the 6- and 8-substituted flavonols were assumed to be attainable. Consequently, 2,4,6-trihydroxy-3-methoxy-ω-benzoyloxy-acetophenone(II) was prepared from iretol (1-methoxy-2,4,6-trihydroxybenzene) and benzoyloxy-

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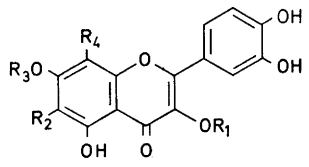


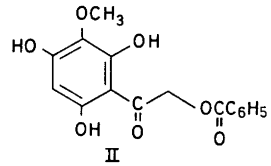
I

Ia R_1=galactosyl, R_2=R_3=H, R_4=OCH_3

Ib R_1=R_2=R_3=H, R_4=OCH_3

Ic R_1=R_3=R_4=H, R_2=OCH_3

Id R_1=R_4=H, R_2=OCH_3, R_3=glucosyl



II

acetonitrile by the Hoesch reaction.[3] Iretol was prepared from picryl chloride.[4] The ketone (II) was condensed with 3,4-di-*O*-benzyl-protocatechuic anhydride [5] by the Allan-Robinson reaction, as modified by Kuhn and Löw.[6] The resulting benzylated flavonol esters were hydrolyzed in glacial acetic acid/concentrated hydrochloric acid to give a mixture of Ib and Ic, as shown by thin layer chromatography and NMR spectroscopy (DMSO-d_6, signals at δ 6.29 and 6.52, corresponding to H-6 in Ib and H-8 in Ic, respectively). (Ref. 7, H-6, δ 6.25—6.28 and H-8, δ 6.45—6.51). The two flavonols were separated by repeated preparative paper chromatography and crystallized from MeOH/H_2O. M.p. 275—277° (Ref. 1, corniculatusin, m.p. 275—277°) and m.p. 264—266° (Ref. 8, patuletin, m.p. 261—263°). In a few cases the analogous 6- and 8-substituted 3-methoxy-flavones have been isolated and, after acetylation, separated by fractional crystallisation (see, *e.g.*, Ref. 2).

During the synthesis purification of all the phenolic compounds by column chromatography on polyamide was shown to be very helpful. The intermediates were characterized by spectroscopic data and m.p. or b.p.

The lower melting flavonol was identified as patuletin (Ic) in the following way: mass spectrum: *m/e* 332 (M^+), 317 (demethylation at 6-OCH_3), 303 (M^+—CHO, involving 3-OH), 167 and 139 (A-ring fragments with 5 and 4 oxygens), 137 and 109 (B-ring fragments with 3 and 2 oxygens).[1] UV (in MeOH) and NMR spectra (of the per-trimethylsilyl ether in CCl_4) were in accordance with Ic. Selective detrimethylsilylation at C-5 gave an upfield shift, 0.16 ppm, (from δ 6.49 to δ 6.33) typical of a C-8 proton.[9] Finally, the IR spectrum was concordant with the spectrum of patuletin.[10]

All data of the synthetic flavonol (Ib) and of the natural aglycone, corniculatusin,[1] were identical, including superimposable IR spectra. The above data clearly distinguish Ic from Ib.

Patuletin has recently been partially synthesized from the glucoside quercetagitrin (Id).[11]

Experimental. Melting points (corrected) were determined on a Leitz hot stage microscope. Column chromatography was performed with polyamide (Woelm), using H_2O, MeOH or mixtures thereof as eluents. The solvent systems for the preparative PC on Whatman No. 3 were: BuOH:AcOH:H_2O (6:1:2) and PrOH:AcOH:H_2O (1:1:1). The IR spectra (KBr discs) were measured on a Perkin-Elmer instrument, type 457, the UV spectra on a Perkin-Elmer instrument, type 402, and the NMR spectra on a Varian A-60 or a JEOL JNM-C-6OHL instrument. The mass spectra were determined by direct insertion technique with an A.E.I. MS902 mass spectrometer, operating at 70 eV and a source temperature of 240°.

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Calculation of the Nearest-neighbour Frequencies in Fragments of Alginate from the Yields of Free Monomers after Partial Hydrolysis

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The chemical inhomogeneity of most heteropolysaccharides and glycoproteins implies that, in general, a quantitative description of the sequence of sugar residues and linkages in these materials can be given only in statistical terms.[1,2] For linear heteropolysaccharides, it may be expressed as a series of conditional probabilities, or near-neighbour frequencies.[2,3] A first step towards a total determination of sequence consists in measurement of the nearest-neighbour frequencies. Methods for doing this have so far entailed measurement of the total homopolymeric fraction,[1] and studies of composition-distribution [3-5] and molecular-weight distribution,[6] in partially degraded materials.

This communication describes a method that consists simply in the measurement of the individual yields of the free monomers after partial hydrolysis to a known degree of scission. Like the other methods, it requires that the kinetics of hydrolysis be understood, and the present application rests upon the finding [7] that the acid-hydrolysis of soluble fragments of alginic acid at 100° can be described, to a good approximation, by two first-order rate-constants, k_M and k_G. These represent the rates at which the two types of monomeric unit, D-mannuronic acid and L-guluronic acid, respectively, are liberated as non-reducing end-groups, and, at pH 2.8, the ratio (k_M/k_G) is 4.3 ± 0.3 (Ref. 7).

Theory. If a linear sequence of monosaccharide residues, A, B, C, D, *etc.* is depolymerised until fractions α_A, α_B, α_C, α_D, *etc.* of the respective monomers are exposed as a specified kind of end-group (*i.e.* either reducing or non-reducing), and if the rate of cleavage of any linkage is independent of the identity of the fragment in which it occurs, then the original sequence can be uniquely determined from the yields (Y_A, Y_B, Y_C, Y_D, *etc.*) of the free monosaccharides and the corresponding values of α, provided that the latter are all different. For example, if the values of α refer to reducing end-groups, and C is the reducing terminal unit, the tetrameric sequence B—A—D—C would give $Y_A = \alpha_A\alpha_B$, $Y_B = \alpha_B$, $Y_C = \alpha_D$ and $Y_D = \alpha_A\alpha_D$, where these yields are expressed as fractions of the amounts of A, B, C, and D, respectively, in the substrate.

When the sequence contains two or more linkages that are hydrolysed at identical rates, or the substrate contains a mixture of different sequences, the system becomes "degenerate", and a unique sequence cannot be determined in this way. Nearest-neighbour frequencies can still be calculated, however, and for relatively long chains, in which end-group effects can be neglected,[6] the calculation is particularly simple.

For a binary linear copolymer, composed of monomeric units M and G, whose hydrolysis is described by two first-order rate-constants as found for the fragments of alginate,[7] the following relationships hold good:[1,4,6]

$$Y_M = F^M[\mathrm{p(MM)}]\alpha_M^2 + (1-F^M)[1-\mathrm{p(GG)}]\alpha_M\alpha_G \quad (1)$$

$$Y_G = F^M[1-\mathrm{p(MM)}]\alpha_M\alpha_G + (1-F^M)[\mathrm{p(GG)}]\alpha_G^2 \quad (2)$$

$$F^M = [1-\mathrm{p(GG)}]/[2-\mathrm{p(GG)}-\mathrm{p(MM)}] \quad (3)$$

where Y_M and Y_G are the yields of monomeric M and G, respectively (calculated as anhydrosugar, and expressed as a fraction of the total weight of starting material); F^M is the mole fraction of M in the starting material; and p(MM) and p(GG) are nearest-neighbour frequencies, defined [2,3] respectively as the fractions of