The limiting slope of Eq. (16) is

$$\frac{d(1/\Lambda S)}{d(c\Lambda Sf^2)_{c=0}} = \frac{1}{K_F\Lambda_0{}^2} + \frac{\alpha^2}{\Lambda_0{}^4} = \frac{1}{K_S\Lambda_0{}^2} \tag{17}$$

whence

$$1/K_S = 1/K_F + \alpha^2/\Lambda_0{}^2 \tag{18}$$

The difference shown in Eq. (18) is a consequence of the *difference* between Θ and γ; in the limit of zero concentration, both Θ and γ approach unity, but as is readily seen from Eqs. (13′) and (15), their difference is linear in concentration, and the mass action extrapolation is essentially one on a linear concentration scale. According to Eq. (3), the ratio α/Λ_0 has the following upper bounds if we set the Walden product $\Lambda_0\eta = 0.5$: $D = 40$, $\alpha/\Lambda_0 \leqslant 2$; $D = 20$, $\alpha/\Lambda_0 \leqslant 4$; $D = 10$, $\alpha/\Lambda_0 \leqslant 8$. Since K decreases[9] rapidly as D decreases, the two methods of extrapolation will not differ significantly when K is less than about 10^{-3}. In the approximate range $10^{-3} \leqslant K \leqslant 1$, however, we recommend extrapolation by means of Eq. (9).

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[9] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, 55, 1019 (1933).

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The Structure of Khellin

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Khellin has been resynthesized by Späth and Gruber from its cleavage product, khellinone, by the application of the Kostanecki–Robinson method.[1] Since this synthesis is not entirely unambiguous, often giving rise to mixtures of the desired chromone and the isomeric 4-methylcoumarin; and since khellin-like model compounds are not unequivocally distinguishable from the corresponding 4-methylcoumarins by absorption spectra, as recent work in this Laboratory has shown, some doubt has remained that khellin actually possesses the 2-methylchromone structure.

Khellin has now been resynthesized from khellinone by two methods which are known to lead unambiguously to 2-methylchromones, and with yields which surpass those usually recorded for the Kostanecki–Robinson reaction. Using a method analogous to that of Wittig,[2] khellinone, treated with sodium hydride in ethyl acetate, yielded a compound (A, see experimental below) which when treated with cold, concentrated hydrochloric acid was converted nearly quantitatively into khellin. The identity of the product was shown by its melting point and mixed melting point with authentic khellin (152–153°), and by analysis.

In a second experiment, khellinone acetate, treated with sodium hydride in ethyl acetate, gave the compound A. This is C-acetylkhellinone, and is converted into khellin by cold, concentrated hydrochloric acid in substantially quantitative yield.

The acylation of substituted *o*-hydroxyacetophenones to yield diketones and, ultimately, chromones is a well-known reaction. 4-Methylcoumarins have not been observed as products of these reactions.

One prior example of the conversion of an *o*-acetoxyacetophenone into the corresponding *o*-hydroxyacetylacetophenone under conditions similar to those used in this work has been recorded.[3] The analogous reaction with *o*-benzoyloxyacetophenones, leading eventually to flavone derivatives, has been used extensively. Model experiments on a number of substituted *o*-acetoxyacetophenones have shown that this procedure is general as a method for the synthesis of 2-methylchromones in good yields.

Details of these reactions and products will be reported in a later publication.

Experimental

Khellinone was prepared in 90% yield by the hydrolysis of khellin in 1% aqueous potassium hydroxide, according to the method of Späth and Gruber.[1]

C-Acetylkhellinone.—(A) To 0.5 g. of khellinone acetate in 5 ml. of dry ethyl acetate was added 0.5 g. of sodium hydride. The solution was warmed gently from time to time for an hour and allowed to stand overnight at room temperature. Crushed ice was added, followed by dilute hydrochloric acid, and the yellow solid collected by filtration. It weighed 400 mg. After recrystallization from aqueous methanol it formed pale yellow needles, which melted at about 90° when plunged into a preheated bath, but at temperatures up to about 122° when heated slowly. It is probable that this behavior is due to a slow dehydration under the influence of heat with the formation of khellin.

Anal. Calcd. for $C_{14}H_{14}O_6$: C, 60.48; H, 5.08. Found: C, 60.34; H, 5.11.

(B) To 0.5 g. of khellinone in 5 ml. of ethyl acetate was added 0.5 g. of sodium hydride. The mixture was allowed to stand overnight and worked up as in (A). The product weighed 413 mg. after recrystallization from dilute methanol.

C-Acetylkhellinone, in dilute aqueous methanol, gives with ferric chloride a momentary flash of green, the color then changing through green-brown to reddish-brown. Khellinone, under identical conditions, gives an intense, pure green.

Khellin.—To 200 mg. of C-acetylkhellinone was added 2 ml. of concentrated hydrochloric acid. The compound dissolved to give a deep orange solution. After solution was complete (about one minute) 20 ml. of water was added. Pure white needles of khellin separated (175 mg.; 94%). After recrystallization from dilute methanol it melted at 152–153° (unchanged by admixture with authentic khellin).

Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.59; H, 4.65. Found: C, 64.48; H, 4.89.

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[1] Späth and Gruber, *Ber.*, 71B, 106 (1938).

[2] Wittig, *Ann.*, 446, 155 (1925).

[3] Virkar and Wheeler, *J. Chem. Soc.*, 1679 (1939).