compound because the acceptor is less reactive and because V must compete for the acceptor with a stronger addendum. A combination of these two factors is probably responsible for the results obtained.

When the dimolecular product from these condensations is not symmetrical, the possibilities of isomerism in the trimolecular product formed from it become extremely complex.[6] In some cases the trimolecular compounds did not melt sharply even when analytically pure, indicating that they were a mixture of isomers. For the purpose of this work, however, it did not seem advisable to examine the isomerism of the products.

Summary

The reactions of simple ketones in the Michael condensation with α,β-unsaturated ketones have been investigated with a view to determining the influence of the structure of the ketone upon its reactivity. The conclusions drawn from the nature and amount of the reaction products are similar to those based on a previous study of addenda possessing two labilizing groups—that is, an increase in substitution about an active methylene group greatly lowers its reactivity and the influence of a methyl group is less than that of the ethyl group.

ITHACA, N. Y. RECEIVED JANUARY 30, 1935

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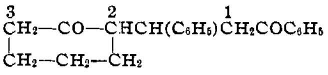
[6] For example, the dimolecular compound (VI) from cyclohexanone and benzalacetophenone may react through the active groups 1, 2 or 3. Reaction at carbon 2 is unlikely because it is so highly substituted. However, reaction at carbons 1 and 3 would give trimolecular products capable of existing in eight and five inactive modifications, respectively.



$\overset{3}{C}H_2—CO—\overset{2}{C}HCH(C_6H_5)\overset{1}{C}H_2COC_6H_5$; $CH_2—CH_2—CH_2$

VI

[CONTRIBUTION FROM THE CITY COLLEGE OF NEW YORK]

The Ultraviolet Absorption Spectra of α- and β-Phenylglucosides

BY DAVID LEWIS

The ultraviolet absorption spectrum of a glycoside is determined by the aglycone residue, since the cyclic sugar group is non-absorbing,[1] or transparent, to the usual limit of investigation, λ = 2200 Å. The purely aliphatic glycosides, such as α-methyl glucoside,[2] β-methyl glucoside,[1] and α-methyl mannoside,[2] show no selective absorption as far as 2300 Å. Aglycones containing a chromophore confer selective absorption on a glycoside. Ramart-Lucas and Rabaté,[1] on the basis of an examination of a series of β-glucosides, have recently shown that such spectra can be classified according to the manner in which the transparent glucosido group is linked to the aglucone. If attached through an aliphatic carbon the positions of the absorption bands nearest the visible are the same for the glucoside and the aglucone, *e. g.*, β-phenylethylglucoside and phenylethyl alcohol. If linked to an aromatic nucleus the bands of the glucoside are displaced to shorter wave lengths and have a smaller intensity as compared to the aglucone, *e. g.*, β-phenylglucoside and phenol. The results reported in this paper show the effect of the configuration of the glucoside link upon this shift.

Experimental

The absorption spectra were obtained with a Hilger rotating sector photometer in conjunction with a Hilger E316 quartz spectrograph. The source of illumination was a condensed spark between iron electrodes. Cells were 1 and 2 cm. The glucosides were examined in water solution of concentration 1.2×10^{-3} *M* and 1.6×10^{-3} *M*. The molecular extinction coefficients were calculated from the equation, $\epsilon = 1/cd \log I_0/I$ where *c* is concentration in moles per liter, *d* is cell length in cm., and $\log I_0/I$ was read on the sector. The results are plotted with log ϵ as ordinates and frequencies as abscissas. Each curve represents about one hundred points.

The glucosides were prepared by deacetylation[3] of the corresponding acetyl glucosides prepared according to Helferich and Schmitz-Hillebrecht.[4] They were recrystallized alternately from water and hydrous ethyl acetate until constant melting point, specific rotation and absorption spectrum were obtained. The constants, after drying at 100°, were: α-phenylglucoside, m. p. 172–172.5° (corr.), $[\alpha]^{30}\text{D}$ +181°; β + phenylglucoside, m. p. 175° (corr.), $[\alpha]^{28}\text{D}$ −72.0°.

Discussion of Results

The curves for the two glucosides are practically identical. Except around the high frequency minimum the differences are within 4 frequency units (10 Å). The curve for β-phenyl-

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[1] Ramart-Lucas and Rabaté, *Compt. rend.*, **196**, 1493 (1933).

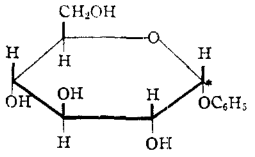
[2] Harris, Hirst and Wood, *J. Chem. Soc.*, 2108 (1932).

[3] Zemplén and Pacsu, *Ber.*, **62B**, 1613 (1929).

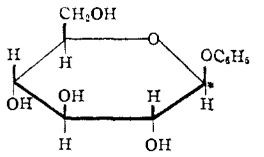
[4] Helferich and Schmitz-Hillebrecht, *ibid.*, **66B**, 378 (1933).

glucoside agrees with that of Ramart-Lucas and Rabaté.[1]

The glucosides may be represented by the symbols



α-Phenylglucoside



β-Phenylglucoside

The arrangement of groups around the glucosidic carbon (marked *) is characteristic of optical enantiomorphs. The α,β configuration as such would not be expected to cause any change in the spectra for Brode and Adams[5] have proved definitely that *d,l* isomers give rise to identical absorption spectra. However, unlike a *d,l* pair of isomers the molecules as a whole are not enantiomorphous since the glucosido group is asymmetric and the same in both. The α,β configuration produces a *cis–trans* arrangement of the chromophoric phenyl group referred to the fixed cyclic sugar residue. Although *cis–trans* compounds give rise to spectra which differ, the bands for the two glucosides are found to be identical. The effect of the glucosidic link on the spectrum of the aglucone is, therefore, independent of configurational effects.

The results are of interest in reference to the views of Ramart-Lucas on the relationship between absorption spectra and chemical reactivity.[6] This investigator has maintained that when compounds containing a given functional group give rise to the same absorption spectra, their velocity of reaction with a common reagent is the same, and that when the spectra differ the velocities differ. In this paper it has been shown that α- and β-phenylglucosides give rise to identical spectra whereas Freudenberg[7] and co-workers report the following hydrolysis constants for the glucosides at 70°: α-phenylglucoside, 37.0 × 10^4; β-phenylglucoside, 13.7 × 10^4.

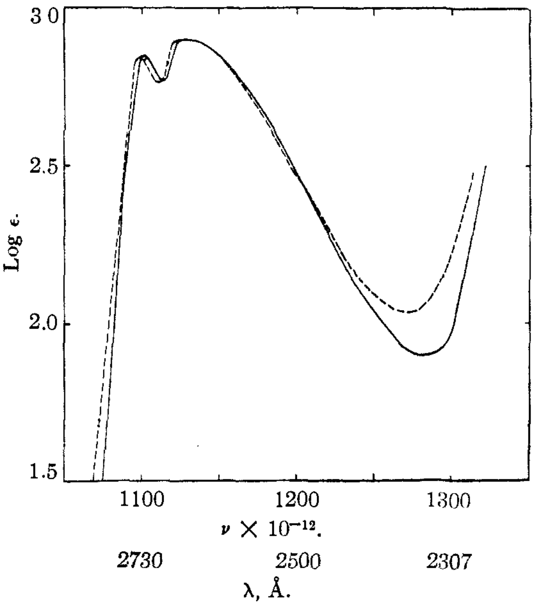


Fig. 1.— — — —, α-Phenylglucoside; ———, β-Phenylglucoside.

The author wishes to thank Dr. H. T. Clarke, College of Physicians and Surgeons, Columbia University, for the use of the spectrographic equipment at his laboratory.

Summary

The ultraviolet absorption spectra of α- and β-phenylglucosides have been determined and found identical. The effect of the glucosidic link upon the spectrum of the aglucone is thus independent of the configuration of the link.

NEW YORK, N. Y. RECEIVED FEBRUARY 2, 1935

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(5) Brode with Adams, THIS JOURNAL, **46**, 2032 (1924); **48**, 2193 (1926).

(6) Ramart-Lucas, *Bull. soc. chim.*, [4] **51**, 289 (1932).

(7) Freudenberg and others, *Ber.*, **61**, 1735 (1928).