terated compounds well into the ultraviolet. On its most sensitive mode the Cary 60 has a precision of ±0.0002°. Measurements were again taken neat. Zero readings were obtained using the corresponding undeuterated and inactive compounds. The instrument was checked by comparison of the O.R.D. of 2-butanol with that reported by Lowry and Allsopp.[7]

The data for each compound were fitted to a single-term Drude equation by a plot of $1/\alpha$ *vs.* λ^2 using values read from the O.R.D. curves at 10-mμ intervals. In general, excellent linear plots resulted from which λ_0 could be obtained by extrapolation. In the example shown in Figure 1 a slight tailing is evident at low wave lengths. In Table I are summarized the experimental values of α at a few wave lengths and the derived values of λ_0.

TABLE I

Compd.	λ_0, mμ	Obsd. rotation, α, in deg.[a] 589 mμ	500 mμ	400 mμ	300 mμ
1-Propanol-1-*d*[b]	205	0.0097	0.0154	0.0262	0.0593
1-Butanol-1-*d*[c]	200	−0.0164	−0.0234	−0.0423	−0.0935
Methyl 1-propyl-1-*d* xanthate[b]	268	−0.0727	−0.1140	...	...
1-Butyl-1-*d* acetate[d,e]	190	0.071	0.104	0.180	...
Benzyl alcohol-α-*d*[f]	245	0.0254	0.0384	0.0736	0.1960[g]
Ethylbenzene-α-*d*[h]	248	0.0462	0.0698	0.1365	0.4350
Benzylamine-α-*d*[i]	263	0.0066	0.0102	0.0208	0.0603[g]
1-Phenylbutane-1-*d*[d,j]	250	−0.103	−0.180	−0.366	...

[a] Rotations were measured on the Cary 60 on the neat liquids at 26° using a 0.1-dm. quartz cell except where noted otherwise. [b] Prepared by V. Sarich (unpublished results) by reduction of propionaldehyde by isobornyloxymagnesium-2-*d* bromide. [c] Older work using a sample prepared by Andreades [A. Streitwieser, Jr., and S. Andreades, *J. Am. Chem. Soc.*, **80**, 6553 (1958)] agreed with that using a different recent preparation of Verbit [A. Streitwieser, Jr., L. Verbit, and R. Bittman, to be published; see Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p. 50N]. [d] The Rudolf polarimeter was used. [e] Prepared by Andreades[c]; 2-dm. tube. [f] Prepared by Wolfe [A. Streitwieser, Jr., and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **79**, 903 (1957)]. [g] At 310 mμ. [h] Prepared by Reif [A. Streitwieser, Jr., and L. Reif, *ibid.*, **86**, 1988 (1964)]. [i] Prepared by Wolfe [A. Streitwieser, Jr., and J. R. Wolfe, Jr., *J. Org. Chem.*, **28**, 3263 (1963)]. [j] A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959); 1-dm. tube. A graph of $1/\alpha$ *vs.* λ^2 gave a curve. An approximate extrapolation was made using a few points at the lowest wave lengths.

The λ_0 parameter should correspond to the wave length of the nearest optically active absorption band, but only approximate agreement may be expected in cases such as ours in which only a single-term Drude equation is used.[8] For 1-butanol-1-*d* and 1-propanol-1-*d*, the λ_0 values of about 200 mμ are substantially higher than the λ_0 values of 157[9] and 154[10] mμ obtained for 2-butanol and 2-octanol, respectively, but are close to an absorption band at 185 mμ in primary alcohols.[11] The aromatic compounds all show λ_0 of approximately 250 mμ. For comparison, 2-phenylbutane has λ_0 = 233 mμ.[12] In other examples it has been shown that the aromatic ring may function as an optically active chromophore.[13]

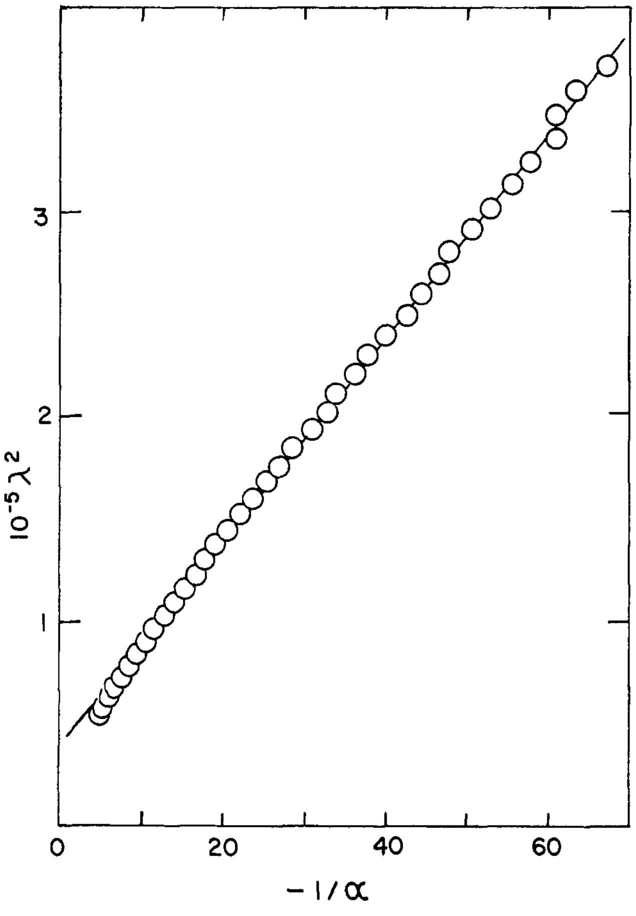

Figure 1.—Drude plot for (−)-1-butanol-1-*d*.

The results of the present work confirm the point of view that deuterium behaves as an ordinary substituent so far as optical activity is concerned.

Acknowledgment.—A few preliminary O.R.D. measurements were made by V. Sarich and L. Reif. We thank Professor I. Tinoco, Jr., for use of the Cary spectropolarimeter and Dr. R. Yolles for his assistance in its use. We are also indebted to Mr. D. Sproul for the use of the modified Rudolf polarimeter.

[7] T. M. Lowry and C. B. Allsopp, *Proc. Roy. Soc.* (London), **A146**, 313 (1934).

[8] See the discussion by W. Heller, "Technique of Organic Chemistry," Vol. I, Part III, A. Weissberger, Ed., 3rd Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 2319 ff.

[9] Obtained with the Cary 60 instrument in the present work.

[10] Calculated from the data of T. M. Lowry and E. M. Richards, [*J. Chem. Soc.*, 1593 (1924)].

[11] A. J. Harrison, B. J. Cederholm, and M. A. Terwilliger, *J. Chem. Phys.*, **30**, 355 (1959).

[12] Calculated from the data of P. W. Benson, J. Kenyon, and J. R. Shepherd [*J. Chem. Soc.*, 658 (1926)].

[13] E. W. Foltz, A. E. Lippman, and C. Djerassi, *J. Am. Chem. Soc.*, **77**, 4359 (1955); G. G. Lyle, *J. Org. Chem.*, **25**, 1779 (1960); L. Verbit, unpublished results.

Tetra-O-methylscutellarein in Orange Peel

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Tangeretin (5,6,7,8,4′-pentamethoxyflavone),[1,2] nobiletin (5,6,7,8,3′,4′-hexamethoxyflavone),[3,4] 3,5,6,7,8,-

[1] E. K. Nelson, *J. Am. Chem. Soc.*, **56**, 1392 (1934).

[2] L. J. Swift, manuscript submitted for publication.

[3] K. Tseng, *J. Chem. Soc.*, 1003 (1938).

[4] L. J. Swift, *J. Org. Chem.*, **25**, 2067 (1960).

3′,4′-heptamethoxyflavone,[5,6] auranetin (3,6,7,8,4′-pentamethoxyflavone),[7] and sinensetin (5,6,7,3′,4′-pentamethoxyflavone)[8-10] have been found in peels or peel oils from tangerine,[1,3] orange,[2,4-10] and grapefruit.[5]

The present contribution is part of a continuing study of orange peel constituents that may affect the flavor of products. It is specifically concerned with the identification of a sixth fully methoxylated flavone, tetra-O-methylscutellarein (5,6,7,4′-tetramethoxyflavone). This is a known compound but, as far as the writer is aware, this is the first report of its occurrence in nature.

Since the flavone was not alkali soluble, it was considered to have no free phenolic or other acidic groups. A negative reaction to ferric chloride and alkalies substantiated this.

Failure of the demethylated flavone to give color or a precipitate with neutral lead acetate indicated no 3-OH group and the absence of *o*-di-OH groups in the B ring. A negative gossypetone test on the demethylated substance showed that either the 5- or 8-positions might be substituted but probably not both. Identification of degradation fragments of the molecule as 6-OH-2,3,4-trimethoxyacetophenone and anisic acid indicated that the flavone possessed methoxyl groups in the 5-, 6-, 7-, and 4′-positions. Final identification depended upon agreement of the infrared spectrum with that of an authentic sample[11] of tetra-O-methylscutellarein when both were run in carbon disulfide solution.

Tetra-O-methylscutellarein was found by Wessely and Moser to exist in two forms melting at 142 and 158–161°.[12] Usually, the higher melting form is obtained, but in the present study, the melting point was found to be 141.9–142.4° (cor.). Herz and Sumi recently obtained a melting point of 163–164° for this compound.[11]

Since the authentic sample was obtained from these investigators and was of the higher melting variety, a mixture melting point determination was not made.

Experimental

In a paper by Swift,[2] a procedure is given for separating the neutral constituents of an extract of orange peel juice. Briefly, this involved extraction of the filtered juice with benzene followed by treatment of the extract with dilute alkali to remove acidic substances and of the resulting extract residue in aqueous–ethanol solution with strong base to decompose lactone substances. After dilution, the neutral substances were extracted with benzene and chromatographed on a Celite column with isooctane equilibrated with acetonitrile. This procedure, with supplementary column chromatography of one fraction, made possible the separation and estimation of the amounts of tangeretin, sinensetin, nobiletin, 3,5,6,7,8,3′,4′-heptamethoxyflavone, and tetra-O-methylscutellarein. In this work, the above-named flavones were found to make up about 80% of the neutral fraction of the benzene extract, tetra-O-methylscutellarein alone amounting to about 9%.

The neutral fraction has been found to vary between 42 and 72% in benzene extracts which, in turn, have been separated from peel juices in amounts ranging from 0.31 to 0.97 g./l.

After recrystallization from ethanol, the tetra-O-methylscutellarein melted at 141.9 to 142.4° (cor.).

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.65; H, 5.30; OCH_3, 36.36; mol. wt., 342.35. Found: C, 66.88, 67.10; H, 5.87; OCH_3, 35.90, 36.20; mol. wt. (mass spectrometer), 342.

The flavone gave negative tests with ferric chloride, Shinoda, and borohydride reagents and its absorption maxima showed no change in position or intensity when sodium acetate was added to a solution in ethanol. The ultraviolet maxima and log ϵ values in absolute ethanol are 216 mμ (log ϵ 4.69), 266 (4.33), and 318 (4.58). The carbonyl absorption band in the infrared region occurs at 1630 cm.$^{-1}$ (KBr). Demethylation was carried out by refluxing 108 mg. of the flavone with 10 ml. of dry benzene and 5 g. of aluminum chloride for 8 hr. The reaction mixture was diluted with water and extracted with ether, and the extract was treated with decolorizing carbon. After filtration, the ether was evaporated, and the residue was recrystallized from a benzene–hexane mixture. Two crops of crystals were obtained, neither of which gave color or precipitate with neutral lead acetate nor a positive gossypetone reaction.

A 34-mg. portion of the original flavone was cleaved by refluxing for 6 hr. with 6 ml. of 10% potassium hydroxide in 50% ethanol. After dilution of the reaction mixture with water, it was extracted with benzene to remove any neutral reaction product. An attempt to form a derivative from this extract was not successful. The remaining alkaline aqueous solution was saturated with carbon dioxide and extracted with benzene to remove the phenolic acetophenone fragment originating in the A-ring. This extract residue gave a 2,4-dinitrophenylhydrazone melting at 174–175°. This agrees well with the melting point of 173° found by Kirby and Sutherland for this derivative of 6-OH-2,3,4-trimethoxyacetophenone.[13] Acidification and extraction of the remaining aqueous solution gave a mixture of acids which were separated on a cellulose column to which a little methyl orange indicator had been added. The development with benzene was continued until the more rapidly moving acid had been eluted. Evaporation of the eluate and recrystallization from hexane gave an acid whose infrared spectrum agreed with that of anisic acid. The final and conclusive evidence was provided by direct comparison of the infrared spectrum in carbon disulfide solution of the isolated flavone with that of an authentic sample[11] in the same solvent.

Acknowledgment.—The author is indebted to Professor Werner Herz of Florida State University for the authentic sample of tetra-O-methylscutellarein and to W. B. Brogden, Jr., of this laboratory, for the mass spectrophotometric determination of the molecular weight. References to specific products of commercial manufacture are for illustration only and do not constitute endorsement by the U. S. Department of Agriculture.

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[5] R. M. Horowitz in "The Orange," W. B. Sinclair, Ed., University of California Press, Berkeley, Calif., 1961, p. 355.

[6] H. Böhme and P. E. Volcker, *Arch. Pharm.*, **292**, 529 (1959).

[7] V. V. S. Murti, S. Rangaswami, and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **28A**, 19 (1948).

[8] See ref. 5, p. 356.

[9] R. Born, *Chem. Ind.* (London), 264 (1960).

[10] L. J. Swift, *J. Food Sci.*, **29**, 766 (1964).

[11] W. Herz and Y. Sumi, *J. Org. Chem.*, **29**, 3438 (1964).

[12] F. Wessely and G. H. Moser, *Monatsh.*, **56**, 97 (1930).

[13] K. D. Kirby and M. D. Sutherland, *Australian J. Chem.*, **9**, 411 (1956).

The Base-Catalyzed Isomerization of the Resin Acids

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The acid-catalyzed isomerization of the conjugated dienic resin acids has been studied.[2] The base-cata-

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[2] W. H. Schuller, R. N. Moore, and R. V. Lawrence, *J. Am. Chem. Soc.*, **82**, 1734 (1960); D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *ibid.*, **78**, 2015 (1956); V. M. Loeblich, D. E. Baldwin, R. T. O'Connor, and R. V. Lawrence, *ibid.*, **77**, 6311 (1955); V. M. Loeblich and R. V. Lawrence, *ibid.*, **79**, 1497 (1957); N. M. Joye, Jr., and R. V. Lawrence, *J. Org. Chem.*, **26**, 1024 (1961).