Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.6; H, 4.6; mol. wt., 520.5. Found: C, 64.9; H, 4.8; mol. wt., 509.0 (in camphor).

Pyrolysis of Compound II.—One-half gram of compound II was heated in a distilling apparatus at 270–280° (bath temperature) under normal pressure. The reaction vessel was left to cool and the substance collected was crystallized from ethyl alcohol and proved to be khellin (m.p. and m.m.p.). Yield, *ca.* 70%.

Thermochromic Behavior in Piperidine.—Compound II dissolved in piperidine (E. Merck), produces a red-violet color at room temperature. The color discharges almost completely on heating. On cooling the red color is regenerated. The phenomenon is reversible for several times, but on standing for a long time at room temperature, the color of the solution fades considerably.

Action of Alumina on II.—When compound II in benzene (thiophene-free and dried over sodium) is treated with a small amount of alumina (Aluminiumoxyd Woelm, alkalifrei, annährend neutral, Akt. Stufe 1, M. Woelm-Eschwege), a red-violet color appears instantaneously on the surface of the inorganic material and the benzene solution remains practically colorless.

The Configurations of Flavan-3,4-diols

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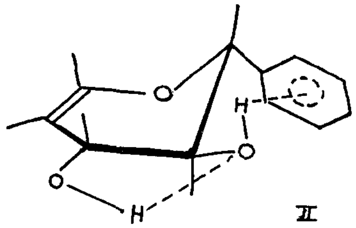
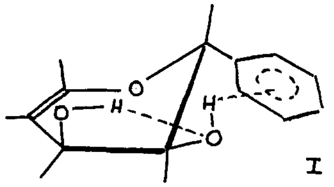
Received July 9, 1962

Corey, Philbin, and Wheeler[2] have recently reported proton magnetic resonance studies on the carbonates and benzoates of two flavan-3,4-diols, the results of which allow an unambiguous assignment of configuration to these two materials. The diol, m.p. 145°, prepared by direct reduction of the 4-ketone has the *trans* relationship of the alcohol functions. The diol, m.p. 160°, which was prepared *via* the oxime followed by reduction to the amine and deamination by nitrous acid possesses a *cis* relationship of the alcohol functions. We now report confirmation of these assignments on the basis of infrared study of the intramolecular hydrogen bonding (H-bonding) in the parent diols.[3]

Infrared spectra of the flavandiols were measured in a saturated solution in carbon tetrachloride (about 0.005 *M*) in a pair of matched, one-cm. silica cells and employing a Beckman DK-1 recording spectrophotometer. The material, m.p. 145°, showed a sharp band at 3608 cm.$^{-1}$. The diol, m.p. 160°, showed a pair of maxima of equal intensity at 3606 cm.$^{-1}$ and 3578 cm.$^{-1}$.



II



I

Consideration of the stretching frequencies to be expected for the several OH...O and OH...π H-bonded species as well as for the free hydroxyl functions permits discussion of the stereo arrangement of the two flavandiols. Benzyl alcohol[4] shows a peak associated with the free alcohol at 3632 cm.$^{-1}$ and a H-bonded (OH...π) peak at 3615 cm.$^{-1}$. Similarly, β-phenylethanols have a free peak near 3630 cm.$^{-1}$ and a bonded peak about 25 cm.$^{-1}$ lower in frequency.[5] The shifts ($\Delta\nu = \nu_{free} - \nu_{bonded}$) in cyclic glycols range from about 30 cm.$^{-1}$ to 103 cm.$^{-1}$ as the projection angle (θ) between the C—O bonds is reduced from near 60° to 0°. Thus the cyclohexane diols with θ near 60° for both the *cis*- and *trans*-diols show similar shifts. The tetrahydronaphthalene-1,2-diols reveal a greater strength of the H-bond in the *cis*- than the *trans*-diol. In the less puckered cyclopentane diols the *cis*-diol shows a strong H-bond, but the *trans*-material shows none. In the bicycloheptanediols[6] with $\theta = 0°$ the shift $\Delta\nu$ is 102–103 cm.$^{-1}$.

The presence of a strong intramolecular OH....O bond at 3578 cm.$^{-1}$ in the isomer with m.p. 160° allows an assignment of a *cis*-configuration to the hydroxyl functions. Chemical evidence[7] which has been confirmed by n.m.r studies[1] shows that the 2-phenyl and 3-hydroxyl groups in the flavandiols are equatorial and *trans*. The diol, m.p. 160°, is therefore represented as at I. The isomer m.p. 145° which must be the *trans*-diol is shown at II.

The sharp band 3608 cm.$^{-1}$ in this latter compound must result from two different O—H stretching frequencies. One involves the π-bonding of the hydrogen atom of the 3-hydroxyl group to the phenyl ring; the other relates to the hydrogen

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[1] Harrison Fellow at the University of Pennsylvania, 1961–1962.

[2] E. J. Corey, E. M. Philbin, and T. S. Wheeler, *Tetrahedron Letters*, No. **13**, 429 (1961).

[3] For development of the method see (a) A. R. H. Cole and P. Jefferies, *J. Chem. Soc.*, 4391 (1956); (b) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).

[4] P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

[5] P. von R. Schleyer, G. Wintner, D. S. Trifan, and R. Bacskai, *Tetrahedron Letters*, No. **14**, 1 (1959).

[6] H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).

[7] R. Bognár, M. Rákosi, H. Fletcher, E. M. Philbin, and T. S. Wheeler, *Tetrahedron Letters*, No. **19**, 4 (1959).

TABLE I

O—H STRETCHING FREQUENCIES OF CYCLIC GLYCOLS AND ARYLALKYL ALCOHOLS (CM.$^{-1}$)

Compound	Free	OH...π	OH...O	Ref.
Benzyl alcohol	3632	3615	...	4
β-Phenylethanol	3631	3604	...	5
cis-Cyclohexane-1,2-diol	3626	...	3587	3b
trans-Cyclohexane-1,2-diol	3634	...	3602	3b
cis-Tetrahydronaphthalene-1,2-diol	...	3618	3575	3b
trans-Tetrahydronaphthalene-1,2-diol	...	3615	3582	3b
cis-Cyclopentane-1,2-diol	3633	...	3572	3b
trans-Cyclopentane-1,2-diol	3620	...	...	3b
exo-cis-Bicycloheptane-2,3-diol	3632	...	3529	6
endo-cis-Bicycloheptane-2,3-diol	3633	...	3531	6
cis-Flavan-3,4-diol (m.p. 160°)	...	3606	3578	
trans-Flavan-3,4-diol (m.p. 145°)	...	3608	...	

atom of the 4-hydroxyl group which is weakly bonded to the oxygen atom in the 3-position. These two frequencies superimpose to give a single sharp band.

Cyanoethylation of Fatty Amines Using Acidic Ion Exchange Catalysis[1]

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Received July 9, 1962

The uncatalyzed addition of acrylonitrile to activated hydrogen bearing molecules is employed to yield the corresponding cyanoethyl substituted derivative. Ionic catalysis aids this addition to less activated centers. Cyanoethylation of weakly basic amines (for example secondary amines already bearing a deactivating cyanoethyl group) has been aided by organic acids such as acetic, propionic, benzoic, or *p*-toluenesulfonic.[2] A mixture of acetic and phosphoric acids has been employed in the direct addition of two moles acrylonitrile to primary fatty amines.[3] Reference 2 suggests use of the organic acid to 10–50% of the combined amine–acrylonitrile weight and the product yield varies from 40–70%.

Acidic ion exchange resins have been found effective in the dicyanoethylation of fatty amines. Since they remain insoluble throughout the reaction, simple filtration removes the resin or resin–amine salt from the final reaction solution. Reuse of the resin has been demonstrated, but a moderate decrease in catalytic activity was noted.

The resins were obtained water-wet and several repeated suspensions in absolute methanol removed most of the water leaving a methanol-wet resin. Similar treatment was given the three types of resins used: Dowex 50W (sulfonic acid type); Rohm & Haas XE-89 (carboxylic acid type); and Chemical Process Co. Duolite C-63 (phosphoric acid type).

Table I (p. 4116) indicates that the sulfonic resin was most active in catalyzing this reaction and the phosphoric acid resin least active.

Experiment 6 represents the repeated usage of the Dowex resin. The weight increase from A to B indicates that some amine–resin salt is combined from the first reaction. The recovered resin was washed twice in absolute methanol and reused immediately. A notable decrease in conversion of primary amine to N,N-dicyanoethyl fatty amine was observed—from 84 to 72%. When used still a third time, no further activity decrease was recorded.

The degree of resin cross linking and the mesh size also appear to affect the degree of dicyanoethylation. Dowex 50W cross linked with 1% divinylbenzene is more effective than resin cross linked with 4, 8, or 12% DVB. Likewise the smaller particle size (50–100 mesh) resin aids this reaction.

Experimental

(Table I, Run 5).—The following materials were placed in a 500-ml. three-neck round-bottom flask with mechanical stirrer, thermometer, and reflux condenser: 177 g. (0.64 mole) of octadecylamine (total amine #205, 97% primary and 0.3% secondary amine, IV 3.5, containing approximately 7% hexadecylamine), 75 g. (1.4 mole) of acrylonitrile, 5 g. of absolute methanol, and 20 g. of methanol-wet Dowex 50W-IX (50–100 mesh) H$^+$ form. An initial exothermic reaction occurred and then external heat was required to maintain the reaction at the reflux temperature of 70–75°. Samples and final reaction mixture were filtered to remove ion exchange resin. The solvent and excess acrylonitrile were removed from the filtrate under reduced pressure and finally at 60° under high vacuum. Nearly quantitative total recovery was achieved.

Hours	Total amine no.	Tertiary amine no.
2	170	22.8
7	161	65
22	157	109
29.5	150	134.7

Theoretical amine no.: dicyanoethyl derivative 149.2; monocyanoethyl derivative 174.0.

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[1] Journal Series Number 312, Central Research Laboratories, General Mills, Inc.

[2] G. W. Fowler and J. W. Lynn, U. S. Patent 3,020,310 (February 6, 1962).

[3] R. Nordgren, U. S. Patent 3,028,415, (April 3, 1962).