tered at τ 1.7 (area 1) and another multiplet centered at τ 2.2 (area 3.2). A small amount of IV was dissolved in concentrated sulfuric acid. Water was added and the resulting precipitate was identified as anthraquinone by comparison of its infrared spectrum with that of an authentic sample.

In another experiment, 19.4 g. (0.100 mole) of anthrone, 39.6 g. (0.366 mole) of sulfur tetrafluoride, and a small amount of anhydrous hydrofluoric acid were heated together in a 185-ml. stainless steel bomb at 75° for 11 hr. and at 98° for 50 min. The crude product was extracted with hexane to give 14.6 g. of dark solid. Sublimation of 3.00 g. of the solid with 76% recovery gave a 48% yield of 10,10-difluoroanthrone, m.p. 100–143°, identified by comparison of its infrared spectrum with that of an analytical sample.

2,6-Di-*t*-butyl-α-(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy radical (VI) was prepared by the method of Kharasch,[6b] oxidation of 4,4′-dihydroxy-3,5,3′,5′-tetra-*t*-butyldiphenylmethane (VII, Ethyl Corporation, antioxidant 702) with potassium ferricyanide, and was used without purification.

Reaction of Anthrone with Sulfur Tetrafluoride in the Presence of Radical Scavengers.—To 9.00 g. (0.0464 mole) of anthrone, purged with nitrogen in a 183-ml. stainless steel reaction bomb, was added 25.2 g. (0.234 mole) of sulfur tetrafluoride, 0.42 g. (0.0010 mole) of VI, 0.31 g. (0.00073 mole) of VII, 70 ml. of methylene chloride, and 0.5 ml. (0.03 mole) of water. The bomb was heated at 70° for 40 min., allowed to remain at room temperature for 23 hr., and then heated at 70° for 19 hr. The bomb contents were extracted with methylene chloride, and the extract was washed with sodium carbonate solution and water, dried, and evaporated to leave 10.3 g. of brown solid. 10,10-Difluoroanthrone (IV), identified by comparison of its infrared spectrum with that of an authentic sample, was obtained with 25% recovery (29% yield) from 1.10 g. of the crude product by sublimation. Of the crude product, 2.00 g. was washed with 3:1 benzene–hexane to leave 0.825 g. of 10,10′-bianthrone (VIII, 47% recovery, 47% yield), identified by comparison of its infrared spectrum with that of an authentic sample. Recrystallization of 0.749 g. of crude VIII from benzene without change in infrared spectrum gave 0.459 g. (29% yield) of a sample, m.p. 263–271° dec., lit.[8] m.p. *ca.* 270–275° dec.

Control for the Reaction of Anthrone with Sulfur Tetrafluoride in the Presence of Radical Scavengers.—A solution of 1.00 g. (0.00515 mole) of anthrone, 0.050 g. (0.00012 mole) of VI, and 0.040 g. (0.000094 mole) of VII in 9 ml. of ethylene chloride was heated at 70–75° for 17.2 hr. The solvent was evaporated to leave 0.934 g. (93%) of anthrone, identified by comparison of its infrared spectrum with that of an authentic sample. Recrystallization from benzene–hexane produced a sample, 0.569 g. (57%), with m.p. 151–167° (no blackening up to 300°), whose infrared spectrum was unchanged.

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(8) J. S. Meek, W. B. Evans, V. Godefroi, W. R. Benson, M. F. Wilcox, W. G. Clark, and T. Tiedeman, *J. Org. Chem.*, **26**, 4281 (1961).

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d-Betuligenol from *Rhododendron maximum* L.

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d-Betuligenol is *d*-4-(*p*-hydroxyphenyl)-2-butanol.[1] The levoratatory enantiomorph, *l*-betuligenol, was first isolated from the bark of the white birch (*Betula alba*) as the β-*d*-glucopyranoside called *betuloside*.[2] Rhododendrin, a glycoside from *Rhododendron fauriae* leaves,[3] and its aglycone, rhododendrol, were subsequently shown to be identical with betuloside and *l*-betuligenol, respectively.[4] It has been unequivocally established that the carbohydrate moiety is attached *via* the aliphatic hydroxyl group.[5] Sosa[1] apparently assumed that the betuligenol he found co-occurring with the glucoside in *Betula alba* was the *l*-form since he reported no specific rotation for it. The isolation of *d*-betuligenol from *R. maximum* in this laboratory was incidental to another investigation, but its occurrence in a species so closely related to one from which the levorotatory isomer had been previously isolated as the glucoside is considered of sufficient interest to warrant this report. The identity of the *d*-betuligenol is established by the data in Table I. Its isolation did not involve conditions which would have hydrolyzed a glucoside.

TABLE I

PHYSICAL PROPERTIES OF BETULIGENOLS

	From betuloside[a]	From *R. maximum*
M.p., °C.	81.5	81–83
$[\alpha]_D$ in ethanol	−18.5° (*c* 3.88)	+17.1° (*c* 2.0)
M.p. of monobenzoate, °C.	68–69	65–66
$[\alpha]_D$ of monobenzoate in ethanol	−12.8° (*c* 1.69)	+14.0° (*c* 1.0)

[a] By either acidic or enzymatic hydrolysis. The data are from ref. 1.

Experimental[6]

Isolation of *d*-Betuligenol.—Fresh *Rhododendron maximum* leaves and twigs (730 lb.) collected in North Carolina in February were ground and extracted by the procedure of Wood, *et al.*[7]

The final chloroform extract was concentrated to a viscous dark green syrup. This was dissolved in 2 l. of methanol–water (9:1) and washed with 2 l. of *n*-hexane. Addition of 4 l. of chloroform to the aqueous methanol layer caused separation of a small aqueous layer, which was discarded. After the solvent was stripped from the methanol–chloroform solution, the 180 g. of dark sirupy residue was dissolved in 500 ml. of ethyl acetate and chromatographed on a column made from 1 kg. of Davison No. 950 silica gel (60–200 mesh) and eluted with ethyl acetate. The first 2.5 l. of eluate collected was concentrated to give 19.1 g. of residue, which was rechromatographed on a similar column of 400 g. of the adsorbent. The first 800 ml. of ethyl acetate eluate gave 12.44 g. of oily crystalline residue. Recrystallization of this from chloroform gave 8.74 g. of *d*-betuligenol having the properties given in Table I.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.07; H, 8.36.

The infrared spectrum (chloroform, Beckman IR 4) contained a sharp hydroxyl band at 2.75 and a broader one near 3.00 μ. An aromatic doublet appeared at 6.20 and 6.25, and a sharp intense band was present at 6.58 μ. The ultraviolet spectrum (ethanol) contained peaks at 224 mμ (ε 7960) and 279 (1910) as well as a shoulder near 284. The compound gave a positive iodoform test.

***d*-Betuligenol Benzoate.**—*d*-Betuligenol (500 mg.) was dissolved in 10 ml. of 10% sodium hydroxide and 1 ml. of benzoyl chloride was added. The reaction mixture was shaken vigorously for 10 min. The white solid which precipitated was removed by filtration, washed thoroughly with water, dried, and recrystallized from cyclohexane. The yield of monobenzoate with the properties recorded in Table I was 410 mg.

(1) A. Sosa, *Ann. chim.* (Paris), **14**, 5 (1940).

(2) A. Sosa, *Compt. rend.*, **196**, 1827 (1933).

(3) R. Kawaguchi, K. G. Kim, and H. K. Kim, *J. Pharm. Soc. Japan*, **62**, 4 (1942); *Chem. Abstr.*, **44**, 9634 (1950).

(4) K. G. Kim, *J. Pharm. Soc. Japan*, **63**, 103 (1943); *Chem. Abstr.*, **45**, 4222 (1951).

(5) G. Zemplen, R. Bognar, and L. Boskovitz, *Ber.*, **77**, 784 (1944).

(6) All melting points were taken on a Kofler stage.

(7) H. B. Wood, Jr., V. L. Stromberg, J. C. Keresztesy, and E. C. Horning, *J. Am. Chem. Soc.*, **76**, 5689 (1954).

4-(*p*-Methoxyphenyl)-2-butanone Semicarbazone.—To 1.0 g. (6.0 mmoles) of *d*-butuligenol in 5 ml. of methanol was added 10 mmoles of diazomethane[8] in 100 ml. of ether, and the resulting solution was left at room temperature overnight, during which time the solution was allowed to concentrate spontaneously. The product was dissolved in chloroform and extracted twice with 0.1 *N* sodium hydroxide. The 555-mg. residue from the chloroform layer would not crystallize, but its infrared spectrum (chloroform) no longer contained the broad hydroxyl band at 3.00 μ. To this product in 12 ml. of pyridine was added slowly a solution of 1.8 g. (18 mmoles) of chromium trioxide in 18 ml. of pyridine. The reaction mixture was stirred 2 hr., 100 ml. of ice–water was added, the resulting solution was acidified with hydrochloric acid, and the product was extracted with chloroform. The 435 mg. of oil thereby obtained afforded a crystalline semicarbazone, m.p. 170–173° (lit[1] m.p. 176°), after recrystallization from a mixture of ethanol and water.

(8) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 166, note 3.

Hydrogen Bonding in 1,4-Substituted Butane-1,4-diols[1]

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An extensive investigation of the hydrogen-bonding propensities of 2,3-substituted butane-1,4-diols demonstrated the utility of the infrared spectroscopic approach to the elucidation of conformational details.[4] This study was restricted intentionally to compounds with no substituents upon the hydroxyl-bearing carbon atoms in order to avoid expected complications: primary, secondary, and tertiary alcohols absorb at different positions in the O–H stretching region of the infrared,[5,6] and all three types of alcohols differ in their proton-donating and -accepting abilities.[6] The present report, dealing with such 1,4-substituted butane-1,4-diols, illustrates the limitations encountered.

Table I summarizes the observed spectroscopic data. The appearance of the free peak followed expectations from literature examples. Primary hydroxyl groups absorbed near 3636 cm.$^{-1}$, secondary hydroxyl groups from 3623 to 3628 cm.$^{-1}$, and tertiary hydroxyl groups from 3611 to 3619 cm.$^{-1}$, normal positions for these types of alcohols.[5,6] For compounds containing only one substitution type (*e.g.*, compounds **1**, **2**, **3**, **6**, **7**, **9**, and **10**) only one free peak was prominent. The other compounds (**4**, **5**, and **8**) showed two free peaks. It is well-known that primary alcohols are the weakest acceptors and the strongest donors, while tertiary alcohols are the strongest acceptors and the weakest donors.[6] In unsymmetrical cases such as the primary–tertiary example (**5**), the major hydrogen-bonding conformation utilizes the primary OH as proton donor and the tertiary OH as acceptor; hence, the 3636-cm.$^{-1}$ band (free primary OH) appears only as a shoulder. Analogous situations are true for compounds **4** and **8**. As suggested by Cole and Jefferies,[5a] spectral shifts (differences in frequencies between free and bonded peaks) in such situations should be measured from the lower intensity free peak.

In our previous study of 1,4-diols, spectral shifts varied from $\Delta\nu$ = 91–196 cm.$^{-1}$.[4] In Table I, despite the changes of substitution type, variations are much less ($\Delta\nu$ = 157–167 cm.$^{-1}$). This illustrates very well the compensating electronic effects of the terminal alkyl substituents on alcohol proton-donating and -accepting abilities.[6] Again, such electron-donating substituents increase the basicity of the adjacent oxygen, but decrease the acidity of the hydroxyl hydrogen. Furthermore, it appears that all of the compounds are quite similar with regard to conformational restrictions and there are no severe steric interactions. Even in the case of the two diastereoisomeric hexane-2,5-diols, very little difference was observed in either $\Delta\nu$ or in the ratio of the integrated free and bonded peak areas (A_f/A_b, Table I).

Besides $\Delta\nu$, the second feature of hydrogen-bonding spectra ordinarily amenable to analysis is the relative areas of the free and bonded peaks. For diols of the same type, these areas should be indicative of the extent of intramolecular association. In the present instance, although only 1,4-diols were examined, the substitution type varied. Therefore, direct comparisons are hazardous, since primary, secondary, and tertiary hydroxyl stretching peaks are known to have different integrated intensities,[5b] in general decreasing with increased substitution. This factor alone should result in a decreased A_f/A_b ratio, provided the bonded peak intensity does not vary similarly with substitution type. In addition, the "*gem*-dialkyl" effect, the increased tendency toward ring formation induced by alkyl substituents,[4] also would be expected to reduce the A_f/A_b ratio (compare compounds **1**, **2**, and **3**). The actual data (Table I) are not particularly revealing. All of the alkyl-substituted diols show A_f/A_b values less than that of the parent, butane-1,4-diol, but in the case of compounds **4** through **10** the cause of this behavior cannot be interpreted with certainty. Even the diastereoisomers (**6** and **7**) show no appreciable difference, despite the fact that the *dl*-compound must have one quasiaxial methyl group on the hydrogen-bonding ring, whatever the conformation of this ring may be.[4]

The hydroxyl stretching peaks for four commercially available 2-butyne-1,4-diols, which compounds served as synthetic precursors for some of the saturated diols, are also given in Table I (**11** to **14**). The spectrum of butyne-1,4-diol, examined previously,[4] showed only one major peak at the abnormal position for primary alcohols, 3610 cm.$^{-1}$. The shift from the usual region was attributed to hydrogen bonding with the π-electrons of the triple bond.[4,7] Compounds **11** to **14** also absorbed from 3610 to 3615 cm.$^{-1}$, but in these instances it is impossible to say with certainty whether these peaks are π-bonded or free. There is very little shift

(1) Paper XII of a series on hydrogen bonding; paper XI, ref. 4. Taken from the Ph.D. thesis of W. F. B., Princeton University, 1964.

(2) American Cyanamid Junior Research Fellow, 1960–1962; National Institutes of Health Fellow, 1962–1963.

(3) Alfred P. Sloan Research Fellow.

(4) L. P. Kuhn, P. von R. Schleyer, W. F. Baitinger, and L. Eberson, *J. Am. Chem. Soc.*, **86**, 650 (1964).

(5) (a) A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 4391 (1956); (b) T. D. Flynn, R. L. Werner, and B. M. Graham, *Australian J. Chem.*, **12**, 575 (1959); (c) C. S. Cook and I. H. Reese, *ibid.*, **14**, 211 (1961).

(6) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

(7) P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *ibid.*, **80**, 6691 (1958).