gave aldehyde **42** as a colorless solid (14 mg, 58%), VPC (15 m, 290 °C, 5.01 min), mp 160–162 °C: IR ($CDCl_3$) 2.76, 3.38, 3.64, 5.80, 6.87, 7.25 μm; ^1H NMR 9.75 (t, 1 H, J = 1.9 Hz), 3.22 (m, 1 H), 2.40 (m, 2 H), 0.98 (s, 3 H), 0.93 (s, 3 H), 0.88 (d, 3 H, J = 5.9 Hz), 0.85 (s, 3 H), 0.77 (s, 3 H), 0.73 (s, 3 H); EIMS m/z calcd 400.3341, found 400.3350; $[\alpha]^{25}_D = +0.56°$ (c = 0.0070 in chloroform). This aldehyde as well as its C-20 epimer **43** was oxygen sensitive and satisfactory combustion analyses were not obtained.

Preparation of *d*-Tirucallol (1c). n-Butyllithium (44 μL, 0.087 mmol) was added to a slurry of isopropyltriphenylphosphonium iodide (38 mg, 0.087 mmol) in tetrahydrofuran (1 mL) at 0 °C. After 10 min at 0 °C, tris[2-(2-methoxyethoxy)-ethyl]amine (4 μL, 0.003 mmol) was added, followed by addition of aldehyde **42** in tetrahydrofuran (0.5 mL). After 10 min at 0 °C, acetone was used to destroy excess ylide and the solvent was removed under reduced pressure. Chromatography on silica gel (3:1 hexane–ether) provided d-tirucallol (**1c**) as a colorless solid (11 mg, 74% yield), VPC (50 m, 280 °C, 9.86 min), mp 130–131 °C: IR ($CDCl_3$) 2.76, 3.38, 3.47, 6.85, 7.24, 8.03, 8.66 μm; ^1H NMR 5.07 (t, 1 H, J = 6.9 Hz), 3.22 (5-line m, 1 H, J = 6.1 Hz), 2.06 (m, 3 H), 1.90 (m, 3 H), 1.66 (s, 3 H), 1.58 (s, 3 H), 0.98 (s, 3 H), 0.93 (s, 3 H), 0.89 (d, 3 H, J = 6.3 Hz), 0.84 (s, 3 H), 0.78 (s, 3 H), 0.73 (s, 3 H); EIMS m/z calcd 426.3861, found 426.3862; $[\alpha]^{26}_D = +4.1°$ (c = 0.0083 in benzene).

Anal. Calcd for $C_{30}H_{50}O$: C, 84.45; H, 11.80. Found: C, 84.34; H, 12.09.

***d*-3β-Hydroxy-5α,13α,14β,17α-lanost-8-en-24-al (43).** The hydrolysis of acetal **41** was performed as described for the hydrolysis of acetal **40** except chromatography was not required to purify aldehyde **43** (43.5 mg, 94%), a colorless foam by VPC (15 m, 290 °C, 4.34 min): IR (film) 2.91, 3.38, 3.45, 3.65, 5.78, 6.82, 7.22, 9.05, 9.66 μm; ^1H NMR 9.76 (t, 1 H, J = 1.8 Hz), 3.21 (dd, 1 H, J = 11.6 Hz, J = 4.6 Hz), 2.40 (m, 2 H), 0.98 (s, 3 H), 0.93 (s, 3 H), 0.86 (s, 3 H), 0.82 (d, 3 H, J = 5.9 Hz), 0.78 (s, 3 H), 0.75 (s, 3 H); EIMS m/z calcd 400.3341, found 400.3331; $[\alpha]^{25}_D = +25.3°$ (d = 0.017 in chloroform).

Preparation of *d*-Euphol (1a). d-Euphol (**1a**) was synthesized by Wittig olefination of aldehyde **43** as described for the synthesis of d-tirucallol (**1c**), providing a colorless solid (22.3 mg, 70% yield) that produced colorless needles from acetonitrile, mp 119–120 °C; VPC (15 m, 290 °C, 4.47 min): IR ($CDCl_3$) 2.76, 3.38, 3.47, 6.87, 7.26, 8.97, 9.11, 9.76 μm; ^1H NMR 5.07 (t, 1 H, J = 7.1 Hz), 3.21 (dd, 1 H, J = 11.6 Hz, J = 5.5 Hz), 2.05 (m, 2 H), 1.88 (m, 4 H), 1.66 (s, 3 H), 1.58 (s, 3 H), 0.98 (s, 3 H), 0.93 (s, 3 H), 0.85 (s, 3 H), 0.83 (d, 3 H, J = 6.2 Hz), 0.77 (s, 3 H), 0.73 (s, 3 H); $[\alpha]^{25}_D = +31.0°$ (c = 0.0104, $CHCl_3$); EIMS m/z calcd 426.3861, found 426.3868.

Anal. Calcd for $C_{30}H_{50}O$: C, 84.45; H, 11.80. Found: C, 84.43; H, 12.07.

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Registry No. **1a**, 514-47-6; **1c**, 514-46-5; (±)-**7**, 124718-18-9; (±)-8, 124718-19-0; (±)-**9**, 124718-20-3; (±)-**10**, 124718-21-4; **11**, 513-81-5; **12**, 53060-22-3; **13**, 3780-51-6; **16**, 124718-22-5; **18**, 124718-23-6; **19**, 124718-24-7; **20**, 28333-62-2; **21**, 124718-25-8; **22**, 124718-26-9; **23**, 124718-27-0; (±)-**24** (isomer 1), 124718-28-1; (±)-**24** (isomer 2), 124718-44-1; (±)-**25** (isomer 1), 124718-29-2; (±)-**25** (isomer 2), 124718-45-2; (±)-**26** (isomer 1), 124718-30-5; (±)-**26** (isomer 2), 124718-46-3; (±)-**27** (isomer 1), 124718-31-6; (±)-**27** (isomer 2), 124718-47-4; (±)-**28** (isomer 1), 124718-32-7; (±)-**28** (isomer 2), 124718-48-5; (±)-**29** (isomer 1), 124718-33-8; (±)-**29** (isomer 2), 124718-49-6; (±)-**30**, 124816-95-1; *l*-**30**, 124816-99-5; **31**, 14495-28-4; **32**, 13879-04-4; **33**, 88199-56-8; **34**, 124718-34-9; **35**, 124754-15-0; **36**, 124718-35-0; **37**, 124718-36-1; **38a**, 124718-42-9; **38b**, 124718-37-2; **39a**, 124718-43-0; **39b**, 124718-38-3; **40**, 124718-39-4; **41**, 124816-96-2; **42**, 124816-97-3; **43**, 124816-98-4; I, 43001-29-2; II, 124718-41-8; IV, 5217-14-1; $CH_2{=}C{=}CH_2$, 463-49-0; (±)-$CH_2{=}C(CH_3)C(CH_3)CH_2Cl(OBu\text{-}t)$, 124718-40-7; euphorbyl acetate, 14787-39-4.

Extraction of Alkanol Isomers

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The isomer effects on the equilibrium partition coefficients of the two propanol, the four butanol, and two of the pentanol isomers between water and immiscible solvents are shown to be governed primarily by the abilities of the alkanols to donate and accept hydrogen bonds. These abilities depend directly on the number of methyl groups bonded to the carbon atom that carries the hydroxyl group. The overall partition coefficient, irrespective of the isomeric form, depends on the total number of carbon atoms in the alkanol via its molar volume. The dependencies on the natures of the extracting solvents are also rationalized in terms of their cohesive energy density, their polarity and polarizability, and their hydrogen bond donation and acceptance abilities.

In a recent paper, Arenson, Kertes, and King[1] reported on the distribution of the four butanol isomers between solutions of m-cresol in n-octane and water. They discussed the effect of the isomeric form of the butanol on the hydrogen-bond formation between it and the m-cresol. They also showed a table of the partition coefficients of the butanol isomers between certain organic solvents and water, in which a systematic decrease of these coefficients for a given solvent in the sequence n-butyl, isobutyl, *sec*-butyl, and *tert*-butyl alcohol is observed. However, they did not discuss this sequence in the absence of m-cresol.

Kertes and King in their review[2] reported the partition coefficients of additional lower alkanols between organic solvents and water, so that a body of data exists that can be interpreted in terms of the isomeric effects for alkanol distribution in general. The distribution of organic solutes between 1-octanol and water in terms of a general linear

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(1) Arenson, D. R.; Kertes, A. S.; King, C. J. *J. Solution Chem.* **1988**, *17*, 1119.

(2) Kertes, A. S.; King, C. J. *Chem. Rev.* **1987**, *87*, 687.

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Table I. Distribution Ratios of the Alkanols[a]

solvent	1-PrOH	2-PrOH	1-BuOH	2-Me-1-PrOH	2-BuOH	2-Me-2-PrOH	1-PeOH	2-Me-2-BuOH
benzene	0.23	0.11	0.66	0.69	0.54	0.24	4.2^b	
	0.204	*0.091*	*0.63*	*0.68*	*0.49*	*0.26*	*2.4*	*1.37*
cyclohexane	0.028	0.017	0.13	0.14	0.11	0.068	0.55^b	0.35^d
	0.032	*0.018*	*0.13*	*0.141*	*0.105*	*0.058*	*0.52*	*0.31*
CCl_4	0.12	0.044	0.51	0.39	0.29	0.14	2.5^b	
	0.081	*0.046*	*0.33*	*0.36*	*0.26*	*0.138*	*2.4*	*0.75*
chloroform	0.40	0.45^b	2.2	2.2^c	2.0^c	1.0^c	11.2^b	
	0.58	*0.45*	*2.2*	*2.4*	*2.0*	*1.5*	*8.2*	*6.6*
ethyl ether	0.95	0.64	4.1	6.9	4.5	2.2	15.8^b	
	1.45	*0.71*	*6.1*	*6.6*	*4.2*	*2.0*	*18.7*	*12.1*
1-octanol	1.8	1.1	7.4^c	5.5^c	4.5^c	2.7^c	25^b	7.8^b
	1.41	*1.12*	*5.3*	*5.8*	*4.3*	*3.5*	*25*	*11.2*

[a] The data in Roman type are from ref 2; unless otherwise noted, those in *italics* type are calculated by eq 1. [b] Reference 8. [c] Reference 1. [d] Reference 9.

Table II. Properties of the Solutes and Solvents

property	1-PrOH	2-PrOH	1-BuOH	2-Me-1-PrOH	2-BuOH	2-Me-2-PrOH	1-PeOH	2-Me-2-BuOH
$v_2/100^a$	0.75_2	0.76_9	0.92_0	0.92_9	0.92_4	0.94_8	1.08_7	1.09_5
π_2^*	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
α_{2m}	0.33	0.31	0.33	0.33	0.31	0.29	0.33	0.29
β_{2m}	0.45	0.51	0.45	0.45	0.48^b	0.57	0.45	0.52^b

property	H_2O	C_6H_6	c-C_6H_{12}	CCl_4	$CHCl_3$	$(C_2H_5)_2O$	n-$C_8H_{15}OH$
$\delta_1^{2\,c}$	2.294	0.353	0.282	0.310	0.380	0.237	0.437
π_1^*	1.09	0.59	0	0.28	0.58	0.27	0.47
β_1	0.47	0.10	0	0.05	0.10	0.47	0.83
α_1	1.09	0	0	0	0.44	0	0.76
A_π	–	0.13	0.41	0.28	0.65	0.14	2.63

[a] In $cm^3/0.01$ mol. [b] See Discussion for explanation of value. [c] In $(kJ/cm^3)^{1/2}$.

solvation energy relationship[3] that involves the molar volume, the polarity/polarizability, and the hydrogen bonding properties of the solutes shows how such an interpretation can be made. This approach was applied to the distribution of organic solutes between water and some 2 dozen water-immiscible organic solvents.[4] The effect of the natures of the solvents for a given solute was discussed in terms of their cohesive energy density, polarity/polarizability, and hydrogen bonding properties.

The expression used[4] for the partition coefficient, log $K_w°$, which is well approximated by the (log of the) distribution ratio of the solute (subscript 2) between the solvent (subscript 1) and water (subscript w) at low concentrations, is:

$$\log K_w° = A_0 + A_\pi(\pi_2^* + 1.1)(\pi_1^* - \pi_w^*) + A_v(V_2/100)(\delta_1^2 - \delta_w^2) + A_\alpha \alpha_{2m}(\beta_1 - \beta_w) + A_\beta \beta_{2m}(\alpha_1 - \alpha_w) \quad (1)$$

The A's should be universal coefficients, independent of the solutes and solvents employed, and A_0 should be zero; this is the case for so-called "dry" solvents, with water contents at saturation $x_w < 0.13$, except that A_π does show a mild solvent dependence, but the term involving it is generally small. The quantity π^* is the Kamlet–Taft polarity/polarizability parameter and 1.1 is used as the correction for the reference solvent of the tabulated π^* values,[5] in order to obtain the absolute value of the π^* of the solute. V is the molar volume, δ is the Hildebrand solubility parameter, and α and β are the Kamlet–Taft hydrogen bond donation and acceptance parameters, respectively.[5] For so-called "wet" solvents, with $x_w > 0.13$, the differences in parentheses in eq 1 between the properties of the (neat) solvents and water are not applicable, and parameters A' are used as coefficients of the solute properties alone.

In the present paper eq 1 is applied to the two isomeric propanols, the four isomeric butanols, and two of the isomeric pentanols, for which there are distribution data in the literature.[1,2] It is shown that the differences in the hydrogen-bonding properties of the isomeric alkanols, depending on the number of methyl groups replacing hydrogen atoms on the hydroxyl-carrying carbon atom, are mainly responsible for the differences noted in the partition coefficients of different isomers of a given alkanol.

Table I shows the partition coefficient data employed, $K_w°$, taken from the review of Kertes and King,[2] unless otherwise noted. The reproducibility of the data is not claimed to be better than 3%. Table II lists the properties of the solutes and solvents. The molar volumes, V, of the solutes at 25 °C and the Hildebrand solubility parameters, δ, of the solvents and water are from the compilation of Riddick et al.[6] The solvatochromic parameters π^*, α, and β of the solvents are from Kamlet at al.[5] The corresponding parameters for the (monomeric) solutes are also from Kamlet and Taft and their co-workers[3,7] with a few exceptions noted in the table and explained in the discussion.

Results and Discussion

The entries in italics in Table I show that eq 1 is able to account quantitatively (within 20%) for the partition

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[3] Kamlet, M. J.; Doherty, R. M.; Abraham, M. H.; Marcus, Y.; Taft, R. W. *J. Phys. Chem.* **1988**, *92*, 5244.

[4] Marcus, Y.; Taft, R. W.; Kamlet, M. J. *ISEC 88 International Solvent Extraction Conference*; Nauka: Moscow, 1988; Vol. III, p 324.

[5] Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877, used for the *solvents* (without subscript m). See ref 3 for the values for the *solutes* (with subscript m).

[6] Riddick, J. A.; Bunger, W. J.; Sakano, T. S. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

[7] Kamlet, M. J.; Taft, R. W., unpublished results, 1987.

[8] Leo, A. J.; Hansch, C. *Pomona College Medicinal Chemistry Data Bank* (unpublished version), 1983.

[9] Mullens, J.; Hanssen, I.; Huyskens, P. *J. Chim. Phys. Physicochim. Biol.* 1971, *68*, 1417.

coefficients of the various alkanol isomers between the "dry" solvents and water, with few exceptions. The values $A_o = 0$, $A_v = -1.79$, $A_\alpha = 7.07$, and $A_\beta = 4.96$ that have been employed are universal, in the sense that they apply to all solutes (not only alkanols) and all "dry" solvents (not just those for which the alkanol distribution data are available).[4] The values of A_π that have been employed are shown in Table II. They are not the same for all solvents, but the size of the term involving them is small (except for the case of the "wet" solvent 1-octanol, see below).

The values of π^* of all the alkanols are the same (0.40), and the molar volumes of the different isomers of a given alkanol differ by at most 2%. Therefore, the appreciable differences noted between the partition coefficients of the isomers must be due to the differences in their α and β parameters. A direct relation exists between the number of methyl groups that are attached to the carbon atom that carries the hydroxyl group of the alkanol and the values of the α and β parameters. As this number increases from 1 to 2 to 3 in the sequence from primary to secondary to tertiary alcohols, the (hydrogen bonding, α) acidity decreases and the (hydrogen bonding, β) basicity increases, due to the inductive effect of the methyl groups. It is, therefore, the ability to donate and accept a hydrogen bond or accept and donate a lone pair of electrons that determines the differences between the partition coefficients of the isomers of alkanols with a given number of carbon atoms.

Some subtelties should be noted in this respect. The α parameter of tertiary pentyl alcohol (2-methyl-2-butanol) has been set equal to that of tertiary butyl alcohol (2-methyl-2-propanol), 0.29, although only two methyl groups are attached to the hydroxyl-carrying carbon atom of the former, contrary to the three attached in the latter. This causes the calculated $K_w°$ of the *tert*-pentyl alcohol for cyclohexane to agree with the experimental value but that for 1-octanol to be too high. The higher value, $\alpha = 0.31$, characteristic of alcohols with only two methyl groups so attached, causes the calculated $K_w°$ for 1-octanol to be even higher but that for cyclohexane to be considerably lower. This is due to the fact that the β parameter for 1-octanol is higher, whereas that for cyclohexane is lower, than that for water.

The β values have been specified by Kamlet and Taft[5] to be 0.45 for primary, 0.51 for secondary, and 0.57 for tertiary alkanols. Adoption of the value 0.51 for 2-butanol, however, produces calculated values of $K_w°$ that differ considerably from the experimental ones, and more compatible values are obtained if the lower value of $\beta = 0.48$ is employed. Again, 2-butanol differs from 2-propanol in that in the former there is only one methyl group attached to the hydroxyl-carrying carbon atom, contrary to the two attached in the latter. This effect is manifested even more strongly in 2-methyl-2-butanol, where $\beta = 0.52$, rather than the 0.57 specified for tertiary alkanols, had to be used. The number of methyl groups seems to be more important for the basicity of the alkanol than for the acidity (see above).

The partition coefficients for the 1-alkanols have been related to the number of carbon atoms in their chains, at least from 1-propanol onward.[2,10,11] Equation 1 operates essentially in the same manner, by specifying linearity of $\log K_w°$ with the molar volume. This representation has been retained here for the sake of generality.[4] Intrinsic volumes,[3] V_I, could have been specified instead of the molar volumes V, requiring only a somewhat different value of A_v, -3.30. The intrinsic volumes of the alkanols, in turn, depend linearly on the number of carbon atoms, with no regard to the isomeric form, at least according to McGowan's expression:[12]

$$V_I = 0.706 + 0.6827(16.73 + 14.09n_C) \qquad (2)$$

where V_I is in cm^3 mol^{-1}, n_C is the number of carbon atoms in the alkanol, and the numbers in the parentheses pertain specifically to the atoms and bonds in alkanols (those outside the parentheses are valid generally).

It should be emphasized that the considerations discussed in this paper pertain to the partition coefficient data, i.e., to the distribution ratios of the isomeric alkanols extrapolated to infinite dilution of the alkanols. It is, therefore, impossible to derive from these data and considerations any information on possible solute–solute interactions (such as dimerization or higher association) that may take place at finite, appreciable concentrations of the alkanol solutes. The water contents of the solvents, again, are the values that pertain to the solvent–water binary system, with no regard to the presence of the solute. Nothing can, therefore, be said about the role of the water content on the solute distribution, since this quantity was not a variable.

Acknowledgment. This paper is dedicated to the memory of Mortimer J. Kamlet, who inspired a large amount of work related to solute–solvent interactions. The research is supported by Grant No. 84-00292 from the U.S.–Israel Binational Science Fund.

Registry No. H_2O, 7732-18-5; CCl_4, 56-23-5; 1-PrOH, 71-23-8; 2-PrOH, 67-63-0; 1-BuOH, 71-36-3; 2-Me-1-PrOH, 78-83-1; 2-BuOH, 78-92-2; 2-Me-2-PrOH, 75-65-0; 1-PeOH, 71-41-0; 2-Me-2-BuOH, 75-85-4; benzene, 71-43-2; cyclohexane, 110-82-7; chloroform, 67-66-3; ethyl ether, 60-29-7; 1-octanol, 111-87-5.

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