240. *Infrared Spectra of Natural Products. Part IX.* Frequencies and Intensities of Hydroxyl Absorption Bands in Triterpenoids and Similar Compounds.*

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Accurate measurements have been made of the hydroxyl stretching frequencies of a number of triterpenoid and similar alcohols in carbon tetrachloride solution. Characteristic frequencies are found for primary (3640—3641 cm.$^{-1}$), axial secondary (3635—3638 cm.$^{-1}$), equatorial secondary (3628—3630 cm.$^{-1}$ at $C_{(3)}$; 3623—3635 cm.$^{-1}$ at $C_{(11)}$), and tertiary (3613—3618 cm.$^{-1}$) hydroxyl groups; it is probable that axial (3617 cm.$^{-1}$) can be distinguished from equatorial tertiary groups (3613 cm.$^{-1}$). Values of the peak apparent molar extinction coefficient, the apparent half band width, and integrated band intensities are given for most of the compounds. The mean value of the integrated intensity is $0{\cdot}60 \times 10^4$ l. mole^{-1} cm.$^{-2}$, and intensities are additive for more than one group in the molecule. Applications of the characteristic frequencies to determinations of organic structure are described.

ALTHOUGH primary, secondary, and tertiary hydroxyl groups have been reported as giving rise to slightly different Raman frequencies,[1] Bellamy has suggested that they cannot be distinguished by means of their infrared absorption,[2] but the examples quoted by him (benzyl alcohol and phenols) are not really typical of primary, secondary, and tertiary alcohols. Jones and Sandorfy [3] similarly doubted whether small frequency differences in this region are suitable for characterising the type of hydroxyl group because of overlap of hydrogen-bonded OH absorption; but this difficulty can be eliminated by using dilute solutions in carbon tetrachloride. We have measured the hydroxyl frequencies and intensities of a number of triterpenoids with primary, secondary, or tertiary groups in axial and equatorial orientations. Results indicating a significant difference in stretching frequency between axial (3637—3639 cm.$^{-1}$) and equatorial (3629—3630 cm.$^{-1}$) 3-hydroxyl groups have been published.[4] In this paper, attention is directed to the differences in frequency between primary, secondary, and tertiary groups, and a few measurements on secondary hydroxyl groups at positions other than 3 are described. Some of these frequencies have been used in interpreting the spectra of *cyclo*hexane-1 : 2-diols.[5]

EXPERIMENTAL

The spectrometer and general experimental conditions have been described.[6] The compounds were studied in carbon tetrachloride solutions at concentrations (<0·005M) too low to

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* Part VIII, preceding paper.

[1] Bateuv and Matveeva, *Izvest. Akad. Nauk S.S.S.R., Otdel. Chim. Nauk*, 1951, 448.

[2] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 86.

[3] Jones and Sandorfy in " Technique of Organic Chemistry " (Ed. Weissberger), Interscience, New York, 1956, Vol. IX, p. 419.

[4] Allsop, Cole, White, and Willix, *J.*, 1956, 4868.

[5] Cole and Jefferies, *J.*, 1956, 4391.

[6] (*a*) Cole and Thornton, *J.*, 1956, 1007; (*b*) Cole and Willix, preceding paper.

allow intermolecular hydrogen-bonding. A background spectrum of absorption by atmospheric water-vapour was recorded through a cell full of solvent on all charts immediately before that of the sample, and the sample spectrum was measured by subtraction of the background at a large number of points. The spectra were run slowly and the spectral slit width at 3630 cm.$^{-1}$ is estimated from the width of the lines in the water-vapour spectrum to be 6 cm.$^{-1}$. In this way peak frequencies can be measured to ± 1 cm.$^{-1}$ and intensities to about $\pm 5\%$.

RESULTS AND DISCUSSION

The hydroxyl frequencies and peak apparent molar extinction coefficients[7] [$\varepsilon = (1/cl) \log_{10} (T_0/T)$] for the individual compounds are given in Table 1 and are summarised

TABLE 1. *Hydroxyl stretching frequencies* (*cm.*$^{-1}$ *in* CCl_4) *and intensity data.*

	ν (cm.$^{-1}$)	$\varepsilon_{max.}$	$\Delta\nu_{\frac{1}{2}}$[a]	$10^{-4}A$
Primary				
Lup-20(29)-en-28-ol	3641	66	24	0·57
3β-Acetoxyolean-18-en-28-ol	3641	60	25	0·54
3β-Acetoxylup-20(29)-en-28-ol	3640	—	—	—
Primary + *secondary* (*equatorial*)				
Lup-20(29)-ene-3β : 28-diol (betulin)	3637	110	34	1·33
Lupane-3β : 28-diol	3636	—	—	—
Urs-12-ene-3β : 28-diol (uvaol) *	3625	107	—	—
Secondary. (i) *Equatorial*[b]				
Olean-18-en-3β-ol (morol)	3629	50	32	0·57
28-Norolean-17-en-3β-ol (oleanol)	3629	53	30	0·57
3β-Hydroxyoleanan-12-one	3628	65	28	0·65
Me 3β-hydroxyolean-12-en-28-oate (oleanolate)	3629	61	32	0·69
Me 3β-hydroxy-12-oxo-oleanan-28-oate	3628	57	—	—
Me 3β-hydroxyurs-12-en-28-oate (ursolate)	3630	54	32	0·61
13 : 27-*cyclo*Ursan-3β-ol (phyllanthol)	3629	59	32	0·67
Lupan-3β-ol	3628	62	27	0·60
Lup-20(29)-en-3β-ol (lupeol)	3629	55	30	0·58
Lanost-8-en-3β-ol	3629	60	30	0·65
Lanost-9(11)-en-3β-ol	3629	64	25	0·57
Lanosta-7 : 9(11)-dien-3β-ol	3629	58	31	0·64
3β-Hydroxylanost-8-en-7-one	3629	55	—	—
3β-Hydroxylanostane-7 : 11-dione	3629	50	34	0·61
3β-Hydroxylanost-8-ene-7 : 11-dione	3629	60	27	0·58
3β-Hydroxylanost-5-ene-7 : 11-dione	3629	60	28	0·60
9 : 19-*cyclo*Eburic-25-en-3β-ol (*cyclo*laudendol)	3629	58	33	0·68
Friedelan-3α-ol (friedelinol)	3630	—	—	—
3β-Acetoxylanostan-11α-ol	3623	50	—	—
7β-Acetoxylanostan-11α-ol	3625	—	—	—
3β : 7β-Diacetoxylanostan-11α-ol	3625	55	—	—
(ii) *Axial*[b]				
Me 3β-acetoxy-19α-hydroxy-12-oxo-oleanan-28-oate	3638	64	—	—
3β : 28-Diacetoxyolean-12-en-19α-ol	3641	—	—	—
Friedelan-3β-ol (*epi*friedelinol)	3635	—	—	—
3β-Acetoxy-12α : 13β-dihydroxyoleanan-28-oic 13-lactone	3624[c]	—	—	—
(iii) *Equatorial* + *axial*				
Me 3β : 19α-dihydroxy-12-oxo-oleanan-28-oate	3633	90	33	1·00[d]
Me 3β : 19α-dihydroxyolean-12-en-28-oate (siaresinolate)	3632	95	35	1·20[d]
Tertiary. (i) *Equatorial*				
3α-Methylcholestan-3β-ol	3613	73	20	0·52
(ii) *Axial*				
3β-Methylcholestan-3α-ol	3617	70	20	0·50
p-Methan-4-ol	3619	—	—	—
(iii) *Miscellaneous*[e]				
Guaiol	3618	—	—	—

* $CHCl_3$ solution. [b] See also Allsop *et al.*[4] and Cole and Michell.[11] [c] See text. [d] Intensity measured by graphical integration to 70 cm.$^{-1}$ on either side of maximum + 15% wing correction. [e] See also Jones *et al.*[9]

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[7] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

TABLE 2. *Characteristic hydroxyl frequencies* (*cm.*$^{-1}$) (CCl_4 *solution*).

Primary	3640—3641	Secondary equatorial	$C_{(3)}$ 3628—3630	Tertiary axial	3617—3619
Secondary axial	3635—3638		$C_{(11)}$ 3623—3625	Tertiary equatorial	3613

in Table 2. In a few cases samples were too small or solubility too low for quantitative measurements. Primary (3640—3641 cm.$^{-1}$) and secondary equatorial (3628—3630 cm.$^{-1}$) groups, the two most common types, can easily be identified by their stretching frequencies. Further, as already pointed out,[4] secondary equatorial groups can be readily distinguished from axial (3637—3639 cm.$^{-1}$), although the latter cannot be differentiated with certainty from primary groups by this means. However, observations at lower frequency [8] might help in the absence of interfering groups (*e.g.*, esters) with strong absorption bands, and oxidation to the corresponding ketone (C=O frequency ~1700—1712 cm.$^{-1}$) or aldehyde (~1730 cm.$^{-1}$) will certainly resolve the pair.

The axial 19-hydroxyl group in the siaresinolic acid derivatives has the same high frequency (~3638 cm.$^{-1}$) as that at position 3, while an equatorial 7-hydroxyl group absorbs just below (~3625 cm.$^{-1}$) its equivalent at position 3. Friedelan-3α- and -3β-ol are consistent with other secondary types with the axial hydroxyl band 5 cm.$^{-1}$ higher than the equatorial.

Tertiary hydroxyl groups do not occur often in triterpenoids, but the spectra of a few similar compounds (Table 1) show that this type of group absorbs near 3618 cm.$^{-1}$ in carbon tetrachloride,[5, 9] and this is easily distinguished from the others. The two methyl cholestanols and *p*-menthan-4-ol show a small difference, in the same sense as for secondary groups, between equatorial and axial hydroxyl groups and, although the number of examples is small, we believe this difference to be significant.

The low hydroxyl frequency (3624 cm.$^{-1}$) of the axial 12α-group in 3β-acetoxy-12α : 13β-dihydroxyoleanan-28-oic 13-lactone is undoubtedly due to the presence of the neighbouring lactone ring. An interaction between the two groups has been reported [6a] in dealing with triterpenoid carbonyl frequencies.

Compounds with more than one type of hydroxyl group absorb at an intermediate frequency [primary + secondary(*eq*) 3636—3637 cm.$^{-1}$; secondary(*eq*) + secondary(*ax*) (3632—3633 cm.$^{-1}$], since the band width (~25 cm.$^{-1}$) is too great for them to be resolved. However, intensity measurements can be used to determine the number of groups present (see below). In practice, low solubility of compounds containing more than two hydroxyl groups will prevent measurements in carbon tetrachloride, but chloroform * may be suitable for triols and tetrols. Hydroxyl frequencies are lower by about 10 cm.$^{-1}$ in chloroform (see uvaol, Table 1, and ref. 11).

Origin of the frequency differences between (a) *primary, secondary, and tertiary groups and* (b) *equatorial and axial groups.* (*a*) The decreasing order of stretching frequencies from primary to tertiary hydroxyl groups can be attributed to a reduction of the bond polarity $-\bar{O}-\overset{+}{H}$ due to the electron-releasing tendency of the C–H bonds of the primary and secondary groups. This is reflected in the known order of increasing acidity of alcohols, *viz.*, primary, secondary, tertiary. The greater electron-density on the oxygen of a tertiary group also gives an explanation for the observation by Cole and Jefferies [5] that in *cyclo*hexane-*trans*-1 : 2-diols, where both hydroxyl groups are equatorial, a secondary hydroxyl group tends to form a hydrogen bond to the oxygen of a tertiary group (cf. I), rather than the reverse.

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* Chloroform, as usually supplied, contains about 0·5% of ethanol as stabiliser and this must be removed.[10]

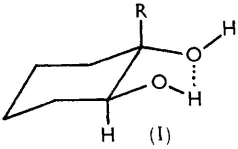
[8] For summary, see ref. 3, p. 433.

[9] Jones, Humphries, Herling, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 2820.

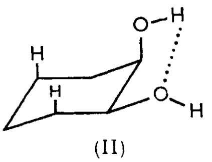
[10] Cole, *Fortschr. Chem. org. Naturstoffe*, 1956, **13**, 17.

[11] Cole and Michell, Part XII of this series, below.

(*b*) The higher stretching frequency of an axial than of an equatorial group appears to be due to steric factors rather than bond polarities. Repulsion of axial hydrogen atoms or other substituent groups would cause an axial hydroxyl group to be oriented about the C–O bond so that its hydrogen would lie on the side remote from the other axial atoms or groups, while an equatorial hydroxyl group is free to assume practically any orientation



(I)



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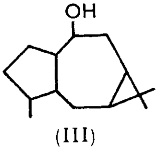
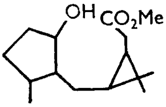


(III)



(IV)

about its C–O bond. Since the oxygen bond-angle is only slightly greater than 90°, the motion of the oxygen atom in the O–H stretching vibration is approximately at right angles to the C–O bond, and in an axial alcohol this is opposed by the repulsion of neighbouring axial groups. This repulsion could easily account for the small increase in force constant and the higher axial frequency (see also the following paper). This hypothesis is supported by the second observation by Cole and Jefferies[5] that in *cyclo*hexane-*cis*-1 : 2-diols, where one hydroxyl group is equatorial and the other axial, the hydrogen of the axial group is bound to the equatorial oxygen atom regardless of whether the groups are secondary or tertiary: this is the only direction in which hydrogen-bonding is possible if the hydroxyl-hydrogen is oriented away from the neighbouring axial hydrogen atoms (cf. II).

Hydroxyl intensities. Peak values of the apparent molar extinction coefficient are given for most of the compounds in Table 1, together with apparent half band widths ($\Delta\nu_{\frac{1}{2}}{}^{a}$). The integrated band intensities [$A = 2{\cdot}303 \times 1{\cdot}55\varepsilon_{\text{max.}}\Delta\nu_{\frac{1}{2}}{}^{a}$ l. mole^{-1} cm.$^{-2}$] have been calculated by Ramsay's method I.[7] The hydroxyl bands are relatively broad compared with others (*e.g.*, for C=O[13] $\Delta\nu_{\frac{1}{2}}{}^{a} = 9$—14 cm.$^{-1}$; for CH_3 bending,[14] 6 cm.$^{-1}$), but they have a shape closely approximating to that of the Lorentz curve. The mean value of the hydroxyl integrated intensity ($0{\cdot}60 \times 10^4$ l. mole^{-1} cm.$^{-2}$) agrees fairly well with results for simple alcohols,[12] and the additivity of the intensities of individual groups is indicated by the results for betulin, methyl siaresinolate, and methyl 3β : 19α-dihydroxy-12-oxo-oleanan-28-oate. There appears to be little difference in intensity between primary, secondary, and tertiary groups. Measurements of peak height will often be sufficient to tell the number of hydroxyl groups in a new compound or degradation product, especially if they are of similar type and absorb at the same frequency. When they are of different kinds, particularly if primary and tertiary, the peak heights will not be additive because of the different positions of the individual bands, and integrated intensities should then be measured.

Applications. The foregoing results have been applied in a number of structural and degradative problems in this laboratory. Phillyrigenin[15] forms two monoacetates with hydroxyl bands (in $CHCl_3$) at 3614 (secondary) and 3625 cm.$^{-1}$ (primary) respectively. Methyl melaleucate[16] (in CCl_4) absorbs at 3629 cm.$^{-1}$ (equatorial secondary), while its 3-epimer obtained by oxidation to the ketone and reduction (Meerwein–Ponndorf) absorbs at 3636 cm.$^{-1}$ (axial secondary). Globulol[17] has a tertiary hydroxyl group (3615 cm.$^{-1}$, in CCl_4), and *apo*aromadendrol (III) (3629 cm.$^{-1}$, in CCl_4) and its degradation product (IV) (3628 cm.$^{-1}$, in CCl_4) both have secondary groups.

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[12] Barrow, *J. Phys. Chem.*, 1955, **59**, 1129; Brown, Sandri, and Hart, *ibid.*, 1957, **61**, 698; Finch and Lippincott, *ibid.*, p. 894; Brown and Rogers, *J. Amer. Chem. Soc.*, 1957, **79**, 577.

[13] Jones, Ramsay, Keir, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 80.

[14] Cole and Macritchie, unpublished results.

[15] Beckwith, Cole, Watkins, and White, *Austral. J. Chem.*, 1956, **9**, 428.

[16] Arthur, Cole, Thieberg, and White, *Chem. and Ind.*, 1956, 926.

[17] Blumann, Cole, Thieberg, and White, *ibid.*, 1954, 1426; Thieberg, Thesis, W. Australia, 1956; Jefferies, Melrose, and White, unpublished results.

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