132. *Infrared Spectra of Substituted Salicylic Acids and Their Esters.*

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The dependence of ester-carbonyl frequencies on the nature of the *O*-alkyl group is briefly discussed. Data are presented for the carbonyl and hydroxyl stretching vibrations of 21 substituted salicylic acids and their methyl esters in dilute solution (carbon tetrachloride). The effects of other solvents are examined.

Alkyl substitution in the 3- and particularly in the 6-position leads to lower carbonyl frequencies: the displacement increases with the bulk of the substituent. The carboxylic-hydroxyl stretching frequencies of the monomeric alkyl-substituted acids are all close to 3530 cm.$^{-1}$ except for the 6-substituted acids examined, in which cases they occur at 3513—3519 cm.$^{-1}$.

This paper describes infrared spectroscopic studies of a series of mono- and di-substituted salicylic acids and their methyl esters. These compounds form a convenient group for the study of environmental effects on a relatively rigid chelated system. Particular attention has been given to nuclear substitution adjacent to the chelated groups, which is known to modify certain biological actions of salicylic acid.[1] The present work appears to be the first deliberate study of the steric enhancement of chelation recently adumbrated by Hunsberger *et al.*[2]

Experimental

Materials.—Many acids were obtained commercially. The following were prepared essentially by published methods: 3-allyl-,[3] 3-propenyl-,[4] 3- and 5-isopropyl-,[5] 5-methyl-,[6] and 6-methyl-salicylic acid.[7] 3-2′-Methylallylsalicylic acid, m. p. 122°, was obtained by thermal rearrangement of *O*-2′-methylallylsalicylic acid.[8] 3-Phenylsalicylic acid was isolated from Eastman " Practical " grade of acid by dissolution in saturated aqueous sodium carbonate (*ca.* 1 equiv.), filtration, precipitation with N-hydrochloric acid (0·8 equiv.), and recrystallisation from ethylene dichloride (charcoal). Sublimation at 0·1 mm. afforded acid of m. p. 186—187·5°: its purity was confirmed by paper chromatography. *o*-Carvacrotic, 3,6-dimethylsalicylic, and 6-methyl-3-t-butylsalicylic acid were kindly supplied by Professor W. Baker, F.R.S., and Dr. W. D. Ollis; 3-t-butylsalicylic acid was generously provided by Dr. O. Fancher (Miles Laboratories, Inc.), 6-ethylsalicylic acid by Dr. R. E. Kent (Chas. Pfizer and Co. Inc.), and 3,5-di-isopropylsalicylic acid by Monsanto Ltd. Methyl esters were prepared with diazomethane: *methyl 3-t-butylsalicylate*, m. p. 47—48° (Found: C, 69·15; H, 7·6. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·75%). Treatment of *O*-methoxycarbonylsalicyloyl chloride with t-butyl alcohol in pyridine afforded t-butyl *O*-methoxycarbonylsalicylate [bands at 1760 and 1720 cm.$^{-1}$; no hydroxyl absorption (liquid film)], hydrolysed by 2N-sodium hydroxide to *t-butyl salicylate*, b. p. *ca.* 180° (decomp.), n_D^{19} 1·5090 (Found: C, 68·0; H, 7·55. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·25%). Samples were carefully purified, finally by sublimation or short-path distillation at 0·1 mm. Purity of liquid samples was checked by gas–liquid chromatography as described elsewhere.[9]

Measurements.—Solvents were purified and spectroscopic determinations carried out by methods previously described.[9] Apparent integrated absorption intensities (β), where

$$\beta = \frac{1}{cl}\int \ln\left(\frac{T_0}{T}\right)_\nu d\nu$$

[1] Andrews, *Brit. J. Pharmacol.*, 1958, **13**, 419; *Biochem. J.*, 1960, **75**, 298; Lightbody and Reid, *Brit. Med. J.*, 1960, I, 1704.
[2] Hunsberger, Gutowsky, Powell, Morin, and Bandurco, *J. Amer. Chem. Soc.*, 1958, **80**, 3294.
[3] Tarbell and Wilson, *J. Amer. Chem. Soc.*, 1942, **64**, 607.
[4] Claisen, *Ber.*, 1912, **45**, 3157.
[5] Croxall, Sowa, and Nieuwland, *J. Org. Chem.*, 1937, **2**, 253.
[6] Jones, *Chem. and Ind.*, 1958, 229.
[7] Eliel, Rivard, and Burgstahler, *J. Org. Chem.*, 1953, **18**, 1679.
[8] Brooks, Stafford, and Young, unpublished work.
[9] Brooks, Eglinton, and Morman, *J.*, 1961, 106.

and c = molarity, l = cell path (cm.), were determined by measurement of optical densities at 5 cm.$^{-1}$ intervals followed by application of Simpson's rule. The solvent–solvent baseline was taken as 100% transmission. For integration, the carbonyl bands were considered to extend over the following regions: acid monomer, +50 cm.$^{-1}$ from the trough between monomer and dimerd acid dimer, −50 cm.$^{-1}$ from the trough; methyl ester, + and −40 cm.$^{-1}$ from the band maximum.

TABLE 1. *Carbonyl and hydroxyl stretching absorptions of esters of benzoic, salicylic and 2,6-dihydroxybenzoic acids* (CCl_4 *solutions*).[a]

Alkyl group of ester	Benzoates			Salicylates			
	ν_{CO}	$\Delta\nu_{\frac{1}{2}}$[a]	ε_a	ν_{CO}	$\Delta\nu_{\frac{1}{2}}$[a]	ε_a	ν_{OH}
Me	1730	11	900	1684	14	665	3210 ‡
Et	1724	14	690	1681	15	655	3200 ‡
Pr^n	1724	13	750	1681 ‡	16	625	3200 ‡
Pr^i	1720	11	855	1678 ‡	20	515	3190 ‡
Bu^t	1717	14	675	1674[b]	13	645	3180 ‡

Alkyl group of ester	2,6-Dihydroxybenzoates						
	ν_{CO}	$\Delta\nu_{\frac{1}{2}}$[a]	ε_a	ν_{OH} (chelated)	ν_{OH} (bonded)	$\Delta\nu_{\frac{1}{2}}$[a]	ε_a
Me	1686	14	730	(3205)[c]	3470 ‡	32	265
Et	1681	17	715	(3195)[c]	3461 ‡	40	275
Pr^n	1680	15	780	(3195)[c]	3456 ‡	30	290

‡ Unsymmetrical band; values in parentheses are approximate.
[a] Approximately 0·0015M-solutions in 0·5 cm. cells (carbonyl region) or 2·0 cm. cells (hydroxyl region). [b] Determined with the Mark II Unicam S.P. 100 (spectral slit width 4 cm.$^{-1}$ at 1650 cm.$^{-1}$). Subsidiary absorption near 3160 cm.$^{-1}$.

RESULTS

Esters.—The effects of substitution in the methyl group of methyl benzoate, methyl salicylate, and methyl 2,6-dihydroxybenzoate were first examined (Table 1). The carbonyl frequency falls as the *O*-alkyl group is changed in the sequence, Me, Et, ≈Pr^n, Pr^i, Bu^t. This order appears to correspond to the inductive effects normally ascribed to these groups,[10] though in the t-butyl esters deformation of the C–CO–O bond angle may contribute to the shift. (Where t-butyl substituents actually adjoin a carbonyl function a marked decrease in frequency is noted.[11]) The centres of the broad hydroxyl bands due to the chelated phenolic groups of the salicylates and 2,6-dihydroxybenzoates show small frequency shifts paralleling the carbonyl displacements. The second phenolic group in the latter esters (I) is bonded to the alkyl-oxygen atom of the ester, and again the frequency is dependent on the *O*-alkyl group, rotation of which is restricted.

The hydroxyl and carbonyl stretching frequencies of a series of methyl esters of substituted salicylic acids are recorded in Table 2. In these compounds the conformation of the ester-carbonyl group is fixed by chelation with the phenolic hydroxyl substituent. Precise measurement of chelate hydroxyl absorption frequencies is precluded by the breadth of the bands. In the 3- and 6-substituted esters it is apparent from superposition of spectra that the band moves to lower frequencies, eventually merging into the C–H absorption region (Fig. a and Table 2). Even where the band maximum is markedly displaced, the region of absorption begins near 3500 cm.$^{-1}$: no such residual " wing " is apparent in the carbonyl absorptions, and the origin of this absorption is obscure: the minor occurrence of carbonyl overtone bands (near 3350 cm.$^{-1}$) could not account for it. The relatively weak chelation in methyl 3-hydroxy-2-naphthoate (no. 21) is reflected in the hydroxyl band at 3266 cm.$^{-1}$ (cf. ref. 12).

Methyl salicylate shows carbonyl absorption at 1684 cm.$^{-1}$ as compared with 1730 cm.$^{-1}$ for methyl benzoate and 1658 cm.$^{-1}$ for the enol form of ethyl 2-oxocyclohexanecarboxylate. Nuclear alkyl substituents not adjoining the functional groups have only minor effects on the carbonyl frequency. Substitution in the 3- and particularly in the 6-position, however, leads invariably to absorption at lower frequencies (see, *e.g.*, Fig. a), the displacement depending on the bulk of the substituent: the bands remain symmetrical in most instances and undergo

[10] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953.
[11] Maroni, *Ann. Chim.* (*France*), 1957, **2**, 757.
[12] Bergmann, Hirschberg, and Pinchas, *J.*, 1950, 2351.

little broadening. This "*ortho*-effect" is conveniently exemplified among the isomers nos. 2, 3, 5, and 13 and in the benzo-analogues 19 and 20. The data observed for esters 19, 20, and 21 are in good agreement with those of Hunsberger *et al.*[13a] A similar steric effect is apparent in methyl 10-hydroxyphenanthrene-9-carboxylate, in which the carbonyl frequency (1649 cm.$^{-1}$) [13b] is much lower than would be expected if only the double-bond character of the 9,10-linkage were considered.[14]

TABLE 2. *Carbonyl and hydroxyl stretching frequencies (cm.$^{-1}$) (CCl_4) [a] in substituted salicylic acids and methyl esters.*

		Ester		Acid			
No.	Substituents	ν_{CO}	ν_{OH} (chelate) [b]	ν_{CO} monomer	ν_{CO} dimer	ν_{OH} of CO_2H (monomer)	ν_{CO} in presence of ether (4% v/v)
1	H	1684	3210	1698	1663	3530	1679
2	4-Me	1681	3200	1697	1662 ‡	3532	1679
3	5-Me	1684	3225	1698	1664	3530	1681
4	5-Pr^i	1684	3230	1698 ‡	1665	3531	1681
5	3-Me	1681	3195	1695	1660	3531	1677
6	3-Pr^i	1679	3180	1693	1659	3531	1678
7	3-Bu^t	1676	(3110)	1691	1657	3530	1670
8	3-Allyl	1682	3185	1695	1660	3530	*
9	3-Propenyl	1682	3170	1693	1660	3529	*
10	3-2′-Methylallyl	1680	3185	1696 ‡	1659	3530	*
11	3-Phenyl	1681 ‡	3155	1695	1660	3528	1675
12	3,5-Pr$^i_2$	1677	3185	1691	1657	3531	1675
13	6-Me	1671 ‡	(3120)	1686	1650	3517	1667 (1660sh)
14	6-Et	1670	(3080)	1683	1649	3515	1665
15	3,6-Me_2	1668 ‡	(3100)	1679 ‡	1641	3518	1658 ‡
16	3-Pr^i, 6-Me	1663	(3040)	1676 ‖	1643 ‖	3518	1660
17	3-Bu^t, 6-Me	1662	(3000)	1671	1639	3519	1658
18	3-Me, 6-Pr^i	1666	(3020)	1677	1640	3514	1657 ‖
19	5,6-Benzo-	1656	(3030)	1668	1641	3513	*
20	3,4-Benzo-	1671	(3065)	1683	1650, 1635	3530	*
21	4,5-Benzo-	1692	3265	1703	1670	3527	*

* Not measured. ‡ Unsymmetrical band. ‖ Irregular contour. sh = shoulder. Values in parentheses are approximate.

[a] Esters were examined as approx. 0·0015M-solutions. The molarity of acids in carbon tetrachloride was 0·0015M (±0·00002M) except for nos. 4 (0·00127M), 19 and 21 (saturated solutions). The solutions in ether–carbon tetrachloride were 0·0015M (±0·00003M) with the exceptions of nos. 15 (0·00073M) and 17 (0·0016M). Measurements were made in 0·5 cm. cells (carbonyl region) and 2·0 cm. cells (hydroxyl region). [b] The frequency values quoted are for the band maxima reasonably attributable to this vibration mode: sharp peaks, sometimes more intense than the bands cited, in the 3000 cm.$^{-1}$ region (C–H stretching absorptions) are ignored. In nos. 7 and 13—20 the appreciable overlap of OH and CH absorptions renders the values approximate, as indicated. Apparent half-band widths ($\Delta\nu_{\frac{1}{2}}{}^a$) were observed as follows. Ester-carbonyl bands, 15 ± 2 cm.$^{-1}$ (except no. 7, 11 cm.$^{-1}$ and nos. 15, 16, and 18, 21 ± 2 cm.$^{-1}$). Ester-hydroxyl bands, approx. 120—570 cm.$^{-1}$, increasing generally through the series with decreasing values of ν_{OH} and ν_{CO}. Acid monomer carbonyl bands, 12 cm.$^{-1}$ (salicylic acid) to 27 cm.$^{-1}$ (no. 16) with a general trend upwards on increasing substitution. Acid dimer carbonyl bands, 15—27 cm.$^{-1}$ with no apparent regularity. Acid carbonyl bands in ether–carbon tetrachloride, 19—29 cm.$^{-1}$. Acid monomer hydroxyl bands, 35 ± 2 cm.$^{-1}$ except no. 21 (29 cm.$^{-1}$).

Frequencies, half-band widths, and intensities (ε_a) of carbonyl absorptions have been determined for some esters in several solvents. The frequency data, summarised in Table 3, show that the solvent shifts for the salicylates are only about half those observed for methyl benzoate, in accordance with the lower carbonyl basicity [9] in the chelated esters. The abnormally small shift for t-butyl salicylate in chloroform is ascribed to steric inhibition of association with the solvent. The half-band widths show some regularities: methyl 3-isopropyl-6-methylsalicylate has the broadest, methyl 3-t-butylsalicylate the narrowest, bands (*e.g.*, $\Delta\nu_{\frac{1}{2}}{}^a$ in hexane 16 and 7 cm.$^{-1}$ respectively). Through the sequence of solvents n-hexane, CCl_4, $CH_3{\cdot}CN$, $CHCl_3$ the half-band widths show a general increase, *e.g.*, methyl 3- and 6-methylsalicylate both have

[13] (*a*) Hunsberger, *J. Amer. Chem. Soc.*, 1950 **72**, 5626; (*b*) Hunsberger, Ketcham, and Gutowsky, *ibid.*, 1952, **74**, 4839.

[14] Bellamy and Beecher, *J.*, 1954, 4487.

$\Delta\nu_{\frac{1}{2}}{}^{a}$ 10 cm.$^{-1}$ in hexane, 23 cm.$^{-1}$ in chloroform. At the same time the intensities (ε_a) generally decrease. For carbon tetrachloride the intensities (ε_a) range from 785 (compound no. 2) to

TABLE 3. *Shifts of ester carbonyl frequencies in different solvents.*

Ester	ν_{CO} (hexane)	$\Delta\nu = \nu_{CO}$ (hexane) − ν_{CO} (solvent) CCl_4	$CH_3{\cdot}CN$	$CHCl_3$
Me benzoate	1735	5	11	15
Me salicylate	1686	2	5	7
Me 3-methylsalicylate	1682	1	4	6
Me 3-t-butylsalicylate	1678	2	5	7
Me 6-methylsalicylate	1672	1	5	6
Me 3-isopropyl-6-methylsalicylate	1666	3	7	8
Bu^t salicylate	1676	2	5	3

370 (no. 18) l. mole^{-1} cm.$^{-1}$. The trend towards lower values with 3,6-disubstitution is accompanied by band-broadening, leading to approximate constancy of integrated intensities ($10^{-4}\beta \sim 3$ l. mole^{-1} cm.$^{-2}$).

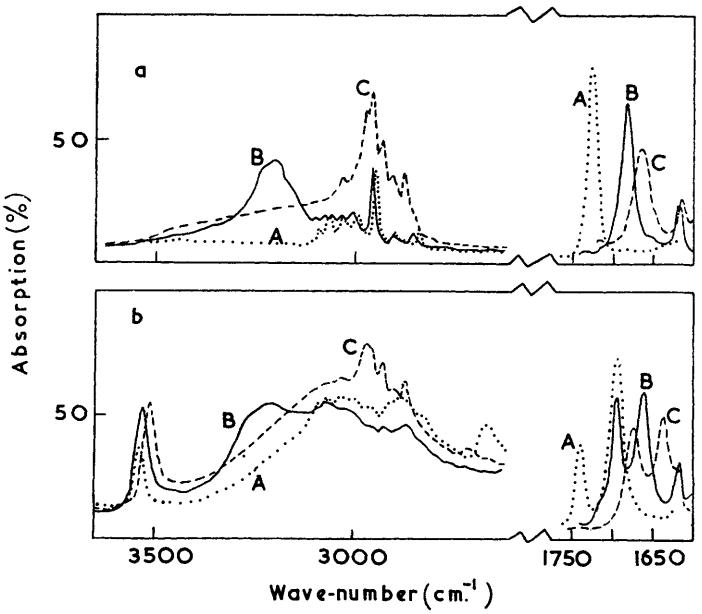


FIG. a. *Methyl esters* (0·00135M *in* CCl_4), 2 *cm. cells* (3650—2600 *cm.*$^{-1}$), 0·5 *cm. cells* (1760—1600 *cm.*$^{-1}$). A, *benzoate*; B, *salicylate*; C, 6-*isopropyl*-3-*methylsalicylate*.

FIG. b. *Acids* (0·0015M *in* CCl_4), 2 *cm. cells* (3650—2600 *cm.*$^{-1}$), 0·5 *cm. cells* (1760—1600 *cm.*$^{-1}$). A, *benzoic*; B, *salicylic*; C, 6-*isopropyl*-3-*methylsalicylic*.

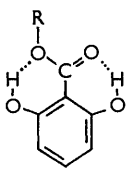
Other Correlations.—In the group of methyl esters examined two intense C–H bands of the ester methyl group occur near 2950 and 2850 cm.$^{-1}$, and are most clearly seen in compounds 19—21 which lack other alkyl groups.

Spectra of methyl esters as liquid films or Nujol mulls will appear in the D.M.S. Index (Butterworths) as spectral cards nos. 6521 onwards. The general absorption patterns are little dependent on the bulk of the substituents; thus the 3,6-dimethyl and 6-methyl-3-t-butyl derivatives exhibit similar spectra with the principal γCH at 804 and 806 cm.$^{-1}$ respectively (cf. 1,2,3,4-tetramethylbenzene, 804 cm.$^{-1}$).[15] In the 6-isopropyl-3-methyl derivative this band is shifted to 820 cm.$^{-1}$. Methyl 6-methylsalicylate simulates the 1,2,3,4-tetrasubstituted compounds in having γCH absorption at 808 cm.$^{-1}$, whereas the 3-alkyl and 3-alkenyl esters show the expected bands near 760 cm.$^{-1}$.

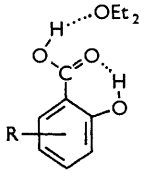
[15] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 2nd edn., 1958.

Acids.—Results recorded in Table 2 refer, with a few exceptions, to 0·0015M-solutions: at this concentration the monomeric and the dimeric species give rise to carbonyl bands of approximately equal intensity in the acids examined. The generally lower proportions of dimeric forms [1 : 1 in the salicylic acids, 2—4 : 1 in unchelated acids [9] (cf. Fig. b)] may be ascribed principally to the reduced carbonyl group basicity. The monomer carbonyl bands are displaced from those of the methyl esters by 13 cm.$^{-1}$ (S.D. 1·2), in close concordance with other substituted benzoic acids.[9,16] The frequency separation between the monomer and the dimer bands (35 cm.$^{-1}$; S.D. 2), however, is significantly lower than that (45 cm.$^{-1}$; S.D. 1·6) observed for unchelated acids. The relatively smaller shift accompanying dimer formation also reflects the lower basicity of the salicylic acid carbonyl group. In the group of acids examined in solutions containing ether, the frequency displacements (−18 cm.$^{-1}$; S.D. 2·5) accompanying formation of the ether-bonded monomers (II) correspond to the value observed for benzoic acid.[9] The concentrations of ether required to eliminate dimer absorption are generally lower than for the benzoic acids, as already noted by Forbes and Knight for ultraviolet absorption.[17] In pure ether (0·5 mm. cells) salicylic acid showed only the band attributed to form (II; R = H): there was no indication of any opening of the chelate ring. The effects of nuclear substitution on the acid-carbonyl frequencies are closely parallel to those described for the methyl ester bands.

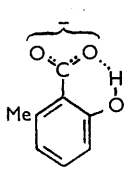
The broad band near 3200 cm.$^{-1}$ due to the chelated phenolic hydroxyl group,[18] and somewhat obscured by the absorption of the acid dimer, is detectable in salicylic acid. It becomes less well defined in the alkyl-substituted acids and is not discernible in no. 17, where it has presumably moved into the C–H absorption region. (Apart from this detail, all the 6-alkyl-acids show similar band outlines between 3600 and 2600 cm.$^{-1}$.) The hydroxyl group of the monomeric acid exhibits a sharp band at a position (3530 ± 3 cm.$^{-1}$) virtually independent of alkyl-substitution at the 3-, 4-, and 5-position but occurring at a lower frequency (3513—3519 cm.$^{-1}$) in all the 6-alkyl-acids examined, and in the naphthoic analogue (no. 19). This feature may have diagnostic value, not merely to locate a 6-substituent, but also to distinguish its type, since within the small group studied the frequency displacement parallels the bulk of the 6-alkyl group.



(I)



(II)



(III)

Apparent extinction coefficients and integrated intensities of the carbonyl absorptions have been measured. The sensitivity of the monomer–dimer equilibrium to minor changes in concentration precludes correlations [19] with pK's within the narrow range of acid strengths represented here. It is sufficient to note that for the acids nos. 1—12, without 6-substituents, the mean value of $\varepsilon_{monomer}/\varepsilon_{dimer}$ is 1·0 (S.D. 0·1) while for the 6-alkylsalicylic acids (nos. 13—18) known or expected to have slightly higher pK's (*e.g.*, no. 13, 3·32; [20] no. 14, *ca.* 3·7,[21]) the ratio is 0·86 (S.D. 0·04). The more marked effect of a greater change in pK is exemplified by 6-chlorosalicylic acid (pK 2·63 [20]) for which the ratio in 0·0015M-solution is 2·0. The ratios of integrated intensities are less reliable, particularly for the 6-substituted acids, in which the displaced dimer bands are close to the region of aromatic C=C stretching absorption (near 1610 cm.$^{-1}$) and may be affected by Fermi resonance. Moreover, the dividing line between the monomer and the dimer bands is difficult to assign with precision. The intensities (ε_a ranging from 575 to 370) observed for the bonded monomeric acids in ether–carbon tetrachloride show a trend similar to, but less well-defined than, that observed for the methyl esters in carbon tetrachloride.

[16] Peltier, Pichevin, Dizabo, and Josien, *Compt. rend.*, 1959, **248**, 1148.
[17] Forbes and Knight, *Canad. J. Chem.*, 1959, **37**, 334.
[18] Martin, *Nature*, 1950, **166**, 474.
[19] Allen and Caldin, *Quart. Rev.*, 1953, **7**, 255.
[20] Bray, Dippy, Hughes, and Laxton, *J.*, 1957, 2405.
[21] Pasternack, Conover, Bavley, Hochstein, Hess, and Brunings, *J. Amer. Chem. Soc.*, 1952, **74**, 1928.

Discussion

The principal feature of the results is the effect of 3- and 6-alkyl substitution. The uniformity of the frequency shifts in the three regions of absorption associated with ester, acid monomer, and acid dimer suggests that the bands are not seriously perturbed by vibrational interaction. The lower frequencies found for 3-alkylsalicylates (nos. 5—7; cf. also nos. 8—11) may be partly due to inductive effects (cf. the shifts of 2 cm.$^{-1}$ on *meta*-methylation of benzoic acid) [9,16] although it should be noted that an opposite effect would ensue from the expected [22a] increase in electron density at the phenolic oxygen atom. The more marked shifts caused by the bulkier 3-alkyl groups are ascribed to the steric enhancement of chelation [2] by compression of the phenolic hydroxyl group, probably with reduction in the O–H · · · O distance. (Similarly, bulky 6-, but not 4-, alkyl substituents strengthen the intramolecular hydrogen bond in substituted 2-bromophenols.[23]) The more striking displacements seen in 6-alkylsalicylates presumably arise from the larger steric requirement of the carboxyl group.

It is difficult to assess from the present work the extent to which the coplanarity of the carboxyl and the phenolic hydroxyl group with the nucleus is disturbed by 3- and 6-substituents. From models it appears that some distortion would occur in all the 6-alkyl derivatives, but there is considerable uncertainty regarding the effective " interference radii " (cf. the apparent coplanarity of the substituents in 1,4-dibromo-2,5-di-t-butylbenzene [22b]). Ultraviolet absorption data are not very informative. Thus, as pointed out by Burawoy *et al.*,[24] the formation of an intramolecular hydrogen bond has little influence on the absorption: salicylic acid and *m*-hydroxybenzoic acid exhibit closely similar spectra in ethanol.[25] Moreover, the introduction of a 6-methyl group causes only a small displacement of the band near 240 mμ, with no appreciable reduction in intensity. Similar small effects are found in the 3,6-dialkylsalicylates: only *o*-carvacrotic acid (no. 18), among those examined, shows an indication of possible steric inhibition of conjugation in the reduced intensities of both the 246 and the 316 mμ absorption.[26] Comparison of carbonyl frequencies for this compound and the 3,6-dimethyl analogue (no. 15) suggests that the limit of steric enhancement of intramolecular hydrogen bonding by 6-alkylation has been reached: it would be desirable to examine a 6-t-butyl-substituted acid. More direct evidence as to coplanarity in these compounds (*e.g.*, from *X*-ray measurements) is required.

Peltier [27] and Dippy and his collaborators [20] have drawn attention to the lower acidity of 6-methylsalicylic acid (pK_a 3·32) than of salicylic acid (pK_a 3·00); the latter authors have ascribed this to inhibition of intramolecular hydrogen bonding. This view does not necessarily conflict with the infrared data, which refer to the undissociated acid; in the (solvated) resonance-stabilised anion (III) small deviations from coplanarity could lead to relative destabilisation with consequent weakening of the acid.

The essentially steric basis of the effects of *ortho*-substitution in benzoic acids is well established (cf. refs. 28, 29): the p*K*'s of *o*-chloro- and *o*-nitro-benzoic acid are respectively 0·9 and 1·3 units lower than those of their *meta*-isomers. That steric effects predominate in 6-substituted salicylic acids is supported by the weakness of 6-chloro- and 6-nitrosalicylic acid, which approximate in strength to their 5-isomers.[20] Moreover, the carbonyl frequency in 6-chlorosalicylic acid is at 1686 cm.$^{-1}$ (monomer), close to that of the 6-methyl

[22] " Determination of Organic Structures by Physical Methods," ed. Braude and Nachod, Academic Press, New York, 1955: (*a*) Brown, McDaniel, and Häfliger, Chapter 14; (*b*) Sutton, Chapter 9.
[23] Brown, Eglinton, and Martin-Smith, unpublished work.
[24] Burawoy and Burawoy, *J.*, 1936, 38; Burawoy and Chamberlain, *J.*, 1952, 2310.
[25] Moser and Kohlenberg, *J.*, 1951, 804.
[26] Brooks, unpublished results.
[27] Peltier, *Compt. rend.*, 1955, 58.
[28] Crawford, *Nature*, 1950, **165**, 728; Ross, *J. Amer. Chem. Soc.*, 1948, **70**, 4039; McDaniel and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3756.
[29] Dippy, Hughes, and Bray, *J.*, 1959, 1717.

analogue despite the different polar character of the substituents. Two hydroxyl bands are observed for 6-chlorosalicylic acid; the first (3508 cm.$^{-1}$) is ascribed to the monomer carboxylic free hydroxyl and the second, weaker absorption (3431 cm.$^{-1}$) to a hydrogen-bonded species. Such bonding is not observed in *o*-halogenobenzoic acids and is attributed to the conformational rigidity imposed by the salicylate chelation.[9]

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The Chemistry Department, The University, Glasgow, W.2. [*Received, August 4th*, 1960.]