152. *The Infra-red Spectra of Organo-phosphorus Compounds. Part III.* Aliphatic Acids and Compounds Related to Natural Products.*

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Structural correlations for the P–OH, P=O, and ionic phosphate groups have been examined for a series of aliphatic organic acids of phosphorus and it has been found that a number of naturally occurring organo-phosphorus compounds show bands in the regions where absorption bands characteristic of these groupings might be expected.

In Part II * correlations were tentatively proposed for a number of structural units of aromatic organic acids of phosphorus. A parallel study has now been made on aliphatic materials; these are of particular interest in the interpretation of the spectra of natural products.

Experimental

The simple compounds whose spectra have been measured were all synthetic products prepared in our laboratories. All were believed to be of reasonably high purity and the phosphorus contents and equivalent weights were checked in all cases. The complex naturally occurring materials examined were kindly supplied by Dr. Malkin, of Bristol University, and these also are believed to be of high purity.

The spectra were obtained by using a Perkin–Elmer 21B recording spectrometer with a rock-salt prism. Liquids were examined as thin capillary films, and solids as pastes in paraffin oil. Where possible, solution spectra in inert solvents were also obtained.

Results

The results obtained are summarised in Table 1 and the spectra are shown in Figs. 1—20. The table also includes a small number of aromatic compounds which have not been reported previously.

(1) *Simple Aliphatic Acids and Salts.*—(a) *The* P=O *vibration.* It has already been shown (Part II) that in the aromatic acids the absorption frequency of the P=O linkage shifts to lower frequencies owing to hydrogen-bonding effects, and that at the same time the intensity is considerably increased. The absorption frequencies for the aliphatic acids now examined are given in Table 1 and it will be seen that a similar effect has been observed in this case. The average absorption frequency is slightly lower than that of the comparable aromatic series, just as the absorption frequencies of the trialkyl phosphates are slightly lower than those of the triaryl phosphates. This probably reflects the difference in the electronegativities of the substituents (Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853).

The assignment of these bands to the bonded P=O vibration is based on the facts that (i) in no instance is there any other band in the 1200—1300 cm.$^{-1}$ region in which the P=O vibration is to be expected (Meyrick and Thompson, *J.*, 1950, 225); (ii) the band vanishes in all cases on formation of the silver salts, and (iii) the OH stretching absorptions indicate that hydrogen bonds of very considerable strength are present.

(b) *The* P–OH *vibration.* The frequency of the P–OH stretching mode is unlikely to be much altered by the substitution of aliphatic for aromatic substituents, and it will be seen from Table 1 that this is the case and that broad absorptions occur in the region 2560—2700 cm.$^{-1}$. A similar absorption has recently been noted by Freidman and Seligman (*J. Amer. Chem. Soc.*, 1951, **73**, 5292) for the half salt of β-naphthyl dihydrogen phosphate.

The broad, shallow absorptions between 1600 and 2500 cm.$^{-1}$ are again present in all the dialkyl phosphates but, as before, the band near 1600 cm.$^{-1}$ occurs only in the disubstituted acids and is absent from the spectra of the monosubstituted products. It would therefore seem likely that this band will afford a useful means of differentiating between mono- and di-substituted materials.

The P–OH deformation mode has been tentatively assigned to the region near 1030 cm.$^{-1}$ in aromatic acids (Part II, *loc. cit.*) but it cannot be observed in these materials owing to the

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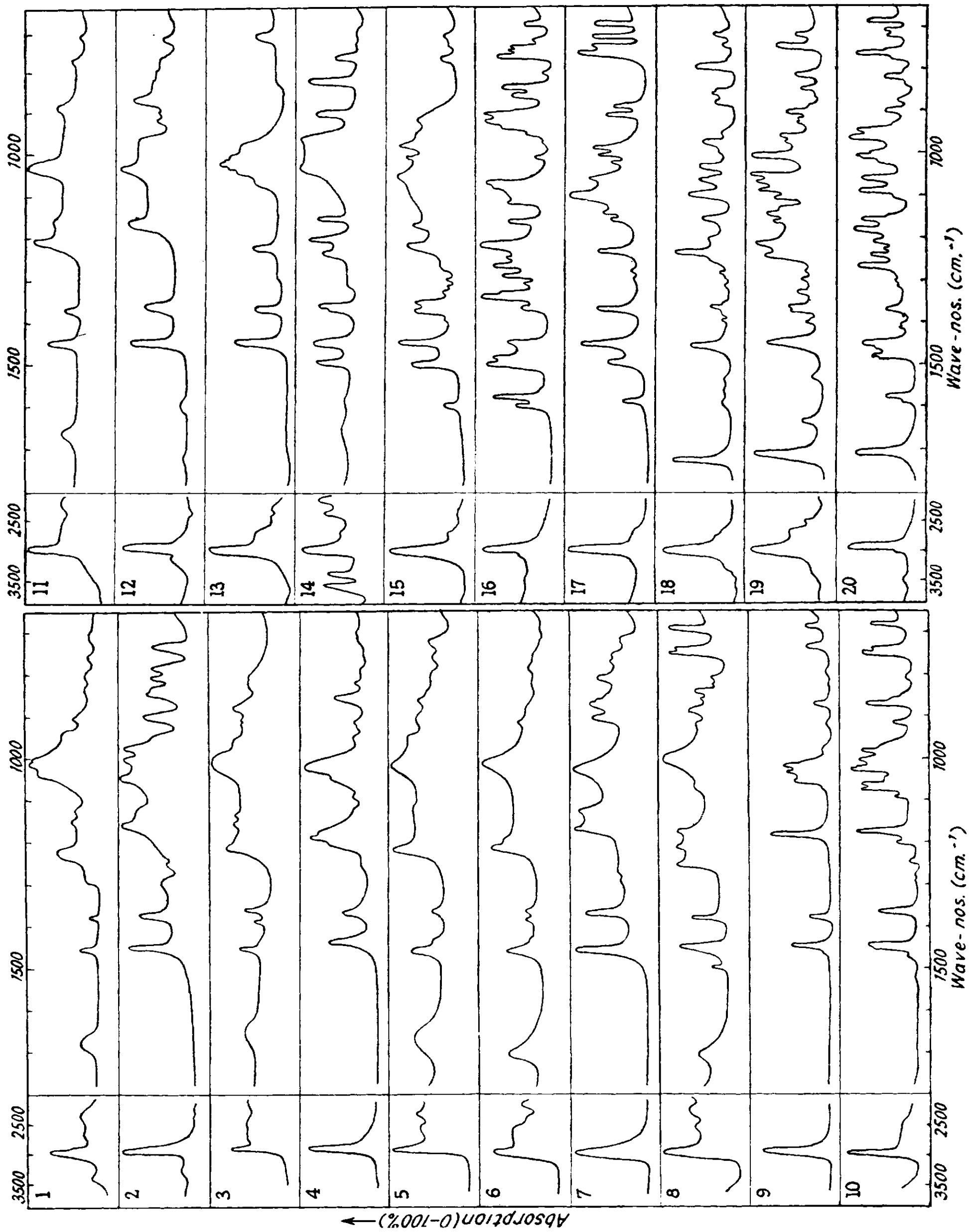
* Part II, *J.*, 1952, 1701.

strong absorption of the P–O–C(aliphatic) grouping at this point. However, many of these compounds show no absorption between the P=O band near 1220 cm.$^{-1}$ and the P–O–C band near 1030 cm.$^{-1}$, so it is reasonable to suppose that the P–OH deformation absorption is superimposed on the P–O–C band in these cases.



(c) *The* P–O–C(*aliphatic*) *vibration.* The assignment of the P–O–C vibration to the 1030 cm.$^{-1}$ region rests upon its invariable occurrence in the large number of such compounds which have been examined by us and by Daasch and Smith (*loc. cit.*), and also upon our observation that the intensity of this band is directly proportional to the number of groups present. Recently, however, Bergmann, Littauer, and Pinchas (*J.*, 1952, 847) have suggested on general grounds that this absorption arises from the unsymmetrical stretching mode of the three alkoxy-groups of trialkyl phosphates. This suggestion is rendered unlikely by the fact that we do not find any substantial alteration in the frequency when one or two of the alkoxy-groups are replaced by hydroxyl groups (Table 1) or by aromatic residues (*J.*, 1952, 475). Similarly, ethyl *NN*-dimethylphosphoramidochloridate (dimethylaminochlorophosphinate) * and related compounds also absorb near 1030 cm.$^{-1}$ (Holmstedt and Larsson, *Acta Chem. Scand.*, 1951, **5**, 1179), so this absorption appears to depend directly on the presence of the P–O–Alkyl group.

Bergmann *et al.* (*loc. cit.*) have found that this band shifts to lower frequencies in branched-chain compounds. We have confirmed their finding that this band is at 996 cm.$^{-1}$ in tri*iso*propyl phosphate, but the effect does not appear to be general, for bis-2-ethylhexyl hydrogen phosphate and di*iso*butyl hydrogen phosphate absorb normally (Table 1), as do a number of branched-chain phosphates and phosphites which we have previously examined.

(d) *The ionic phosphate vibration.* With the aromatic organic acids of phosphorus, salt formation results in the disappearance of the P═O band and its replacement by a band in the 1050—1100 cm.$^{-1}$ region which we have tentatively ascribed to the ionic phosphate vibration. A similar effect is found with the aliphatic acids except that, as will be seen from Table 1, the frequency shift is very much less marked and the ionic phosphate absorption occurs in the 1150 cm.$^{-1}$ region. This indicates that the P–O bond length is shorter in the aliphatic than in the aromatic salts. Like that of the P═O vibration, therefore, the ionic phosphate frequency is liable to shift with alteration in the electronegativity of the substituent groups, but in this case the effect is very much more marked.

Dibenzyl hydrogen phosphate is interesting in that its silver salt shows two bands, at 1081 and 1180 cm.$^{-1}$, both of which are absent from the free acid. The lead salt, however, shows only the 1180 cm.$^{-1}$ band, which is therefore the ionic phosphate absorption. Frequency changes have been observed in some other substances on substitution of the lead for the silver salt but these are small in all cases.

(e) *The* 980 *cm.*$^{-1}$ *region.* Bergmann *et al.* (*loc. cit.*) suggested that an absorption they observed near 980 cm.$^{-1}$ in trialkyl phosphates may arise from the in-phase symmetrical vibration of the three alkoxy-groups. This band is particularly interesting owing to its intensity and to the fact that it appears in a very high proportion of the organo-phosphorus compounds we have examined. However, the same objections apply to this suggestion as to the similar one relating to the unsymmetrical mode, in that the frequency remains essentially unchanged on replacement of all the alkoxy-groups by aromatic residues or on the replacement of one or two of them by hydroxyl groups or by chlorine. The absorption occurs in all those compounds we have examined which contain the residue $>$PO·O$^-$ or $>$PS·O$^-$ regardless of the nature of the substituents, and it is very largely absent from compounds in which these groups are absent. The intensity also appears to be related to the number of P–O–R groups present. It occurs in triphenyl phosphate but is absent from triphenyl phosphite, and it is present also in ethyl *NN*-dimethylphosphoramidochloridate (Holmstedt and Larsson, *loc. cit.*) and absent from bisdimethylaminofluorophosphine oxide. We would therefore prefer to regard it as being essentially related to a P–O stretching mode of a quinquevalent phosphorus atom.

The 1030 cm.$^{-1}$ band would then be regarded as arising essentially from the O–C link of the P–O–C skeleton, whereas the 980 cm.$^{-1}$ band would arise from the P–O link. This would explain satisfactorily the occurrence of the 1030 cm.$^{-1}$ band at the same position as that in which it is found in ethers and in Si–O–C compounds, and would also explain why only the former is affected if the ether carbon atom is unsaturated whilst only the latter is affected if the valency state of the phosphorus atom is changed. However, it is difficult to see why two frequencies as close as these do not show more interaction. The band also shows an inexplicable variation in intensity in a few cases. In nearly all the compounds examined it is exceedingly strong but it is relatively weak in tributyl phosphate and some other higher trialkyl phosphates. Its intensity is also reduced in many of the dialkyl hydrogen phosphates. In all the aromatic compounds the band vanishes on salt formation or is much reduced in intensity, indicating its dependence upon the presence of the P═O

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* The names now used are those agreed upon by the Chemical Society and the American Chemical Society (cf. *Proc.*, 1952, 138): the older British names are added in parentheses.

group. With aliphatic materials, a weaker band often persists in the same general region which, coupled with the reduced intensity of the band in the free acid, makes these results indecisive. More work will be required before the origin of this interesting band can be adequately defined.

TABLE 1.

		Assignments (cm.$^{-1}$)				
Fig.	Phosphate	P-OH (St.)	1600—2500	P=O	$\text{P}\langle^{\text{O}^-}_{\text{O}^-}$	P-O-C
1	Di-*n*-butyl hydrogen	2600	1665, 2280	1220	—	1025
2	Silver di-*n*-butyl	—	—	—	1152	1026
3	Di*iso*butyl hydrogen	2580	1665, 2160	1213	—	1028
4	Lead di*iso*butyl	—	—	—	1184	1028
5	Di-*n*-amyl hydrogen	2590	1665, 2290	1210	—	1030
6	Di*iso*amyl hydrogen	2600	1665, 2220	1212	—	1030
7	Lead di*iso*amyl	—	—	—	1175	1030
8	Dibenzyl hydrogen	2560	1695, 2270	1250	—	1036
9	Lead dibenzyl	—	—	—	1180	1036
10	Silver dibenzyl	—	—	—	1180	1036
11	Bis-2-ethylhexyl hydrogen	2560	1665, 2260	1212	—	1022
12	Silver bis-2-ethylhexyl	—	—	—	1162	1032
13	Octadecyl dihydrogen	2500—2700	2240	1230	—	1025
14	*p*-Octylphenyl dihydrogen	2660	2220	1235	—	—
15	Lead *p*-octylphenyl	—	—	—	1054	—
16	Lead di-*p*-nitrophenyl	—	—	—	1078	—
17	Lead phenyl	—	—	—	1100	—

(2) *Natural Products and Related Substances.*—The spectra of three αα′-disubstituted kephalins have been published by Baer, Maurukas, and Russell (*J. Amer. Chem. Soc.*, 1952, **74**, 152) but they have not discussed them in relation to the vibrations associated primarily with the phosphorus residue. We have now examined a small number of materials to see how far the correlations so far derived can usefully be applied to such materials. The spectra of αα′- and αβ-dilauroylkephalin and of αβ-distearoyl-α′-glyceryl diphenyl phosphate are shown in Figs. 18—20 respectively, and the tentative assignments we have made relating absorption bands to structural units for these and other materials are given in Table 2. It is emphasised, however, that in substances of such complexity it is not possible to make definite assignments, and the only purpose of this table is to show that absorptions do, in fact, occur at the frequencies at which they might be expected from our work on simpler compounds.

TABLE 2.

	Assignments					
Compound	P-OH (St.)	1600—2500	P=O	P-O-C	C=O	C-O
αα′-Dilauroylkephalin	2500—2700	2350	1228	1026	1730	1100 1166
αβ-Dilauroylkephalin	2510—2670	2090	1224	1010 1059	1718 1733	1112, 1175 1156
αβ-Dilauroylkephalin, silver salt	Nil	Nil	Nil	1022 1053	1727	1080 1150—1180
αβ-Distearoyl-α′-glyceryl dihydrogen phosphate	2650	2150	1229	1050	1704 1733	1080 1176, 1190
αβ-Distearoyl-α′-glyceryl diphenyl phosphate	—	—	1271	1005 1060	1738	1087 1160, 1168
αα′-Dipalmitoyl-β-glyceryl *NN*-diphenylphosphorodiamidate (dianilinophosphinate)	—	—	1220	1026	1739	1093, 1163

DISCUSSION

The assignments of the P–OH stretching modes can be regarded as being reasonably certain, for few other substances absorb in these regions. The shallow band in the range 2300—2100 cm.$^{-1}$ was also noted in all cases. The other band near 1660 cm.$^{-1}$, observed in monobasic acids, could not now be observed owing to masking by the C=O absorption. The occurrence of the P–OH absorption in the kephalins is interesting, since it indicates that, in contrast to the lecithins, they do not exist in a zwitterion form. This is suggested by the fact that the NH_2 stretching and deformation absorptions also appear in the normal regions. These bands do not occur in the zwitterion benzyl hydrogen phosphoramidate (aminophosphonate), and OH and NH_2 absorptions are also absent from the spectra of the common amino-acids (cf. Randall, Fowler, Fuson, and Dangl, " Infra Red Determination of Organic Structures," Van Nostrand, 1949). The co-existence of the OH and NH_2 groups in the same molecule may be due to the fact that the OH group is already strongly hydrogen-bonded.

The absorptions of the P=O and P–O–C groups are difficult to differentiate from those of the glyceride C–O stretching absorptions. Shreeve, Heather, Knight, and Swern (*Analyt. Chem.*, 1950, **22**, 1498) have shown that triglycerides give a typical pattern of strong absorption near 1163 cm.$^{-1}$, flanked by weaker bands at 1250 and 1100 cm.$^{-1}$. The first and last of these are readily recognisable in these spectra and they have been assigned accordingly. However, the band near 1230 cm.$^{-1}$ in all acidic materials is very much stronger than either of these and we have accordingly assigned it to the bonded P=O absorption. This is supported by the disappearance of the band in the silver salt of αβ-dilauroylkephalin and by the fact that in αβ-distearoyl-α′-glyceryl diphenyl phosphate, in which hydrogen bonding of the P=O cannot occur to the same extent, only a weak band occurs in this region and a strong P=O absorption occurs near 1270 cm.$^{-1}$. None of these other substances with bonded P=O groups shows any absorption in the range 1250—1300 cm.$^{-1}$.

The assignment of the P–O–C absorption is also rendered difficult by the presence of these C–O absorptions and also by the possible appearance of P–OH deformation bands. We have assigned the P–O–C absorption as being the strongest band near 1030 cm.$^{-1}$, and it is noteworthy that no strong absorptions occur in this region in any of the triglycerides described by Shreeve *et al.* (*loc. cit.*).

The doubling of the C=O absorption in the two αβ-acids does not occur in the corresponding αα′-acids and this may be an indication that one of the two carbonyl groups of the αβ-acids is more strongly hydrogen-bonded than the other. The P–OH group may be involved in this bonding since only a single band is shown in αβ-distearoyl-α′-glyceryl diphenyl phosphate in which the OH groups are substituted. If this preliminary observation should be confirmed on examination of further members of this series, it might afford a rapid method for differentiating between αα′- and αβ-glycerophosphoric acids.

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