899. *The Isomerisation of Deca-2 : 4-dienoic Acid* * *in Presence of Alkali at* 180°.

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When deca-2 : 4-dienoic acid is heated with potassium hydroxide at 170—180° the conjugated diene system is moved away from the carboxyl group. A complex mixture of diene acids is produced; in this conjugated diene unsaturation predominates, although to a minor extent non-conjugated diene acids are also present. At equilibrium the main products, apart from about 15% of unchanged deca-2 : 4-dienoic acid, appear to be decadienoic acids with conjugated unsaturation in the 4 : 6- and 5 : 7-positions.

In earlier communications dealing with the component acids of stillingia oil from the seeds of *Sapium sebiferum* Roxb. and *S. discolor* (Crossley and Hilditch, *J. Sci. Food Agric.*, 1950, **1**, 292), and with the constitution of the deca-2 : 4-dienoic acid (*idem, J.*, 1949, 3353) which forms about 5% by weight of the total acids of these oils, it was recorded that in alcohol this acid exhibits maximum absorption in the ultra-violet region at about 260 mμ. It was also remarked that when the acid is heated at 170—180° with alkali (as required for the spectroscopic determination of linoleic and linolenic acids; Hilditch, Morton, and Riley, *Analyst*, 1945, **70**, 68) this absorption band is gradually replaced by that with a maximum at 234 mμ characteristic for conjugated diene unsaturation in an aliphatic chain. The present communication deals with further studies of the changes involved.

When a dilute solution of methyl deca-2 : 4-dienoate in ethylene glycol was heated at 180° with the same proportion of potassium hydroxide (11·7 g. per g. of acid) as that used in alkali-isomerisation for spectrophotometric determination of linoleic or similar acids, the extinction coefficient at the new band head (234 mμ) reached a maximum value after 3 hours. The products then formed were almost completely acidic, less than 1% being neutral: the shift of the absorption band is not therefore due to decarboxylation. The acidic products, on fractional distillation at reduced pressure, left about 15% of dark, non-volatile, polymerised acids. The distilled acids, apart from traces of acids of low molecular weight, were of uniform molecular weight closely approximating to that (168) of decadienoic acids; no hydroxy-acids could be detected. The ultra-violet absorption curve of the main fraction of the distilled acids showed $E^{1\%}_{1\,\text{cm.}}$ 1280 at 234 mμ and 227 at 260 mμ. The value of $E^{1\%}_{1\,\text{cm.}}$ for deca-2 : 4-dienoic acid at 260 mμ is 1427 (Crossley and Hilditch, *loc. cit.*), whilst $E^{1\%}_{1\,\text{cm.}}$ for other decadienoic acids (calculated from that of octadeca-9 : 11-dienoic acid) is about 2000. The observed extinction coefficients of the main fraction of distilled acids thus correspond approximately with a mixture of about 15% of unchanged deca-2 : 4-dienoic acid and about 60% of other conjugated decadienoic acids, leaving a balance of about 25% which presumably consists of decadienoic acids in which the double bonds have become non-adjacent.

Next, the methyl esters of the main fraction of distilled acids were oxidised with potassium permanganate in acetone. Quantitative examination of the monobasic acid products (cf. p. 4614) indicated that their composition was approximately :

	Acetic	Propionic	Butyric	Pentanoic	Hexanoic
% (by weight)	8	30	27	14	21
% by (mol.)	11	35	26	12	16

The molar proportion of hexanoic acid corresponds with the amount of unchanged decadienoic acid observed spectrophotometrically in the isomerised products: when this is disregarded, the proportions of acids with unsaturation terminating respectively at carbon atoms 9, 8, 7, and 6 of the decadienoic chain are roughly 13, 42, 31, and 14%.

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* Geneva nomenclature ($CO_2H = 1$).

Alkali-isomerisation in ethylene glycol at 180° of linoleic (octadeca-9 : 12-dienoic) acid gives a mixture of the 9 : 11- and 10 : 12-dienoic acids, whilst linolenic (octadeca-9 : 12 : 15-trienoic) acid yields mainly the 10 : 12 : 14-isomer (Dann and Moore, *Biochem. J.*, 1933, **27**, 1166; Moore, *ibid.*, 1937, **31**, 138; 1939, **33**, 1635; Kass, Miller, and Burr, *J. Amer. Chem. Soc.*, 1939, **61**, 482); but no other substantial migration of double bonds appears to take place in these instances, although of course the possibility of a minor movement of the conjugated systems cannot be wholly excluded without a much more detailed analytical study. Thus the behaviour of the octadecapolyenoic acids contrasts sharply with that of deca-2 : 4-dienoic acid, and it appears that the terminal carboxyl group in a long-chain fatty acid exerts relatively little influence on the mobility of double bonds in the chain if the latter are separated from it by several methylene groups.

A specimen of deca-2 : 4-dienol, prepared by reduction of deca-2 : 4-dienoic acid with lithium aluminium hydride, gave in *cyclo*hexane solution an absorption band with a sharply-defined maximum ($E^{1\%}_{1\,\text{cm.}}$ 1340) at 231 mμ. Replacement of the carboxyl by the carbinol group thus displaces the band-head of conjugated dienoic acid at 260 mμ to the position characteristic for the conjugated diene system in an aliphatic chain.

EXPERIMENTAL

Methyl deca-2 : 4-dienoate was prepared from stillingia oil as previously described (Crossley and Hilditch, *J.*, 1949, 3353). The ester (7 g.) was heated at 175—180° for 3 hours in ethylene glycol (400 ml.) in which potassium hydroxide (80 g.) had been dissolved, it having been ascertained that after this time the extinction coefficient of the absorption band at 234 mμ reached a maximum value. The isomerisation was performed in a round-bottomed flask attached to an air-condenser and heated in an oil-bath, the flask being frequently shaken to ensure complete solution and hydrolysis of the ester. The product was isolated by pouring the cooled reaction mixture into water, acidification with dilute sulphuric acid, and extraction of the acid products with ether.

In a preliminary experiment the recovered isomerised acids were converted into methyl esters and fractionally distilled at atmospheric pressure through a semimicro fractionating column. The esters (2·6 g.) yielded four fractions (in all 1·7 g.), the equivalents of which lay between 182·7 and 185·6 (calc. for methyl decadienoate, 182), with a residue of 0·9 g. of polymerised material. In a further experiment the acids from the alkali isomerisation of 7 g. of methyl deca-2 : 4-dienoate were fractionated (without reconversion into esters) under reduced pressure; in addition to a first fraction of 0·3 g. (equiv., 160·8) and a polymerised non-volatile residue of 1·0 g., there was obtained a main fraction of 5·9 g. (equiv., 168·7. Calc. for decadienoic acid, 168). In solution in alcohol this fraction exhibited an absorption band in the ultra-violet spectrum with a well-defined maximum at 234 mμ ($E^{1\%}_{1\,\text{cm.}}$ 1280) and $E^{1\%}_{1\,\text{cm.}}$ of 227 at 260 mμ. These acids were examined for the presence of hydroxy-acids with negative results.

Oxidation of the Methyl Esters of the Isomerised Acids.—The esters (4 g.), heated under reflux in solution in acetone, were oxidised with powdered potassium permanganate (40 g. necessary for complete oxidation). The product, after removal of acetone and addition of water, was decolorised with sulphur dioxide and the resulting acidic liquor was steam-distilled. The dibasic acids in the residual liquid were insufficiently soluble in ether for quantitative extraction, and examination of the acidic products was confined to those which were volatile in steam. The condensate from the steam-distillation was exhaustively extracted with alcohol-free ether, and the bulk of the ether removed; the acids left in a small volume of ether were dried (Na_2SO_4) and then washed into a small flask connected to a semimicro fractionating column, through which they were distilled at atmospheric pressure from an oil-bath which was finally allowed to reach 200°, giving the following fractions :

No.	g.	Bath temp.	Equiv.	No.	g.	Bath temp.	Equiv.
1	0·16	160—180°	102·6	4	0·41	190—210°	94·9
2	0·23	180—185	75·8	5	0·33	Residue	137·0
3	0·30	185—190	82·2				

Fraction 1 (containing small proportions of water and ether) and fraction 2 yielded a *p*-bromophenacyl ester, m. p. 53° [mixed with *p*-bromophenacyl propionate (m. p. 60°), 56°]. Fraction 1 was, for purposes of calculation, taken as propionic acid, whilst fraction 2 was calculated from its equivalent as a mixture of propionic and butyric acids. Fractions 3 and 4 were similarly calculated as mixtures of butyric and valeric acids, whilst the residue was assumed to be hexanoic acid. The acids (0·10 g.; mean equiv., 89·2) left in the filtered sodium sulphate were calculated as a mixture in the same proportions as those disclosed by the results of the fractional distillation. The acid left unextracted in the aqueous liquor and the traces which distilled during removal of the ether (together 0·13 g. as acetic acid) consisted largely of acetic acid, as shown by the production of ethyl acetate when the potassium salts were warmed with ethyl alcohol and sulphuric acid, but minor amounts of propionic acid may also have been present.

The data obtained are thus only sufficient for a rough estimate of the proportions of the monocarboxylic acids present, but indicate amounts of the order given on p. 4613 when calculated according to the assumptions mentioned.

Deca-2 : 4-*dienol.*—Freshly-powdered lithium aluminium hydride (2·2 g.) was heated under reflux in carefully dried ether (250 ml.) for 1½ hours with occasional stirring, after which deca-2 : 4-dienoic acid (10 g.) in solution in dry ether (150 ml.) was added during about 15 minutes, the mixture being then refluxed with constant stirring for an hour. The cooled mixture was slowly added to cold water (500 ml.) to which dilute sulphuric acid was subsequently added. The ethereal solution so obtained was washed several times alternately with dilute alkali solution and with water, whereupon crude deca-2 : 4-dienol (8·9 g.) was obtained. On fractionation at 0·2 mm. the main fraction (about 80% of the whole) distilled at 67° as a colourless liquid which, in solution in alcohol, showed a marked absorption band in the ultra-violet spectrum with maximum at 231 mμ ($E^{1\%}_{1\,\mathrm{cm.}}$ 1340).

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