534. *Urea Complexes of Some Branched-chain and Cyclic Esters.*

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The interaction of forty branched-chain and cyclic esters with urea has been examined and the minimum chain length necessary for complex formation has been determined. It is emphasised that the minimum chain-length is intimately related to the spatial configuration, and the principles for determining whether any particular ester will form a complex have been deduced.

THE original discovery that urea forms complexes with straight-chain organic compounds (Bengen, G.P. Appl. 12438/1940) has been more fully described by Bengen and W. Schlenk (*Experientia*, 1949, **5**, 200) and by W. Schlenk (*Annalen*, 1949, **565**, 204). This work has been extended by Redlich, Gable, Dunlop, and Millar (*J. Amer. Chem. Soc.*, 1950, **72**, 4153), Holman and H. Schlenk (*ibid.*, p. 5001), and Newey, Shokal, Mueller, Bradley, and Fetterly (*Ind. Eng. Chem.*, 1950, **42**, 2538). W. Schlenk (*loc. cit.*) reported that this property was not confined to straight-chain compounds; branched-chain and even cyclic compounds form complexes provided that the straight-chain portion of the molecule is long enough. Only two examples were given, namely, benzene and 3-methylheptane which do not form addition complexes whereas *n*-octadecylbenzene and 3-methyleicosane do.

Linstead and Whalley (*J.*, 1950, 2987) showed that under suitable conditions certain branched-chain and cyclic esters could be separated from similar straight-chain esters in almost quantitative yield. It was found that methyl 3-methylundecanoate formed a complex while ethyl methylsuccinate, methyl β-methylglutarate, *iso*propyl adipate, methyl ββ'-dimethylsuberate, methyl salicylate, and ethyl benzoate did not. They pointed out that branched-chain esters failed to give stable complexes unless there was a long straight-chain sector in the molecule. Zimmerschied, Dinerstein, Weitkamp, and Marschner (*Ind. Eng. Chem.*, 1950, **42**, 1300) confirmed that the linearity of the alkyl chain is a predominant factor, derivatives of slightly branched alkanes being able to form adducts if the straight portion is long enough. It appeared to them that two methyl groups or an ethyl or a phenyl side-group could prevent complex formation altogether. They found that the *iso*propyl esters of oleic, eicos-11-enoic * and docos-13-enoic acids, methyl 12-methylmyristate,* and 12-methyltetradecyl acetate formed complexes, whereas 1-methylheptyl acetate, *iso*propyl 12-methylmyristate, methyl 9-phenylstearate, and 2-ethylhexyl myristate did not.

In order to permit this technique to be used for the separation of material (*e.g.*, wool wax) containing straight-chain, branched-chain, and cyclic molecules, a more systematic investigation into the minimum length of the anchor necessary to enable a particular group to be held in a complex has been carried out. Contrary to the statement by Zimmerschied *et al.* compounds containing an ethyl side chain or a phenyl group can be made to give complexes provided that certain spatial requirements are fulfilled.

The importance of the configuration is well illustrated by the amyl alcohol series where the minimum carbon chain-length of the acid necessary to enable the ester to form a complex ranges from two atoms to ten. The carbonyl group, though somewhat larger than a methylene group, does not hinder complex formation. The introduction of a side-chain methyl group leads to a slight increase in the cross-sectional area if it is on the same side of the molecule as the carbonyl oxygen atom, and to a larger increase if it is on the opposite side.

Ester derived from	Minimum carbon chain length of acid †	Total straight chain
n-Amyl alcohol	2 (acetate)	8
3-Methylbutanol	6 (hexanoate)	11
2-Methylbutanol	10 (decanoate)	15

† Including the oxygen atom of the C–O–C grouping.

Ester derived from	Minimum chain length from nucleus.†	Ester derived from	Minimum chain-length from nucleus.
Phenol	9 (octanoate)	Phenylacetic acid	13 (decanol)
Quinol	2 × 5 (dibutyrate)	*cyclo*Hexanol	13 (dodecanoate
Benzyl alcohol	12 (decanoate)	Benzoic acid	(20 not sufficient)

† Including the oxygen atom of the C–O–C grouping.

In the series containing an aromatic nucleus, benzoic esters provide an example of the cross-sectional area becoming too large for the space available.

Comparison of the behaviour of derivatives of quinol and phenol, *iso*amyl alcohol and 1-methylheptanol, and 2-ethylbutanol and 2-ethylhexanol, shows that the effectiveness of the straight portion is not appreciably diminished if it is in two separate parts.

It may appear at first sight that isomers could be separated by using suitable derivatives. However, a compound that does not form a complex by itself may give a mixed complex in the presence of one that does, *e.g.*, 3-methylheptane gives a mixed complex with *n*-octane (W. Schlenk). Linstead and Whalley have shown that the converse may occur; a compound that normally forms a complex may be prevented from doing so by the presence of one that does not. In either case only a partial separation will be achieved. This is demonstrated further by the amyl alcohol series. By itself 3-methylbutyl hexanoate forms an addition product, but not in the presence of 2-methylbutyl hexanoate. Conversely, 2-methylbutyl octanoate, normally unable to form an adduct, gives a mixed addition product with 3-methylbutyl octanoate. In the latter case, however, the 3-isomer is preferentially removed by urea and, for a counter-current process, the enrichment factor is large enough to allow the separation of optically active amyl alcohol from a mixture containing *iso*amyl alcohol.

Members of a homologous series may be partially separated by treating the mixture with less than the equivalent amount of urea. For example, a mixture containing equal quantities of

* Geneva nomenclature ($CO_2H = 1$) is used throughout the paper.

octadecyl dodecanoate and octadecyl palmitate can be separated into four fractions of which the one with the highest affinity for urea contains 75% of palmitate and that with the lowest affinity only 14%. Qualitative results are given in the following table.

Complex-forming.	Unable to form complexes.
n-Octadecyl acetate	*n*-Octadecyl benzoate
n-Octadecyl dodecanoate	
n-Octadecyl palmitate	Cholesteryl acetate
Dioctadecyl sebacate	Cholesteryl octanoate
	Cholesteryl palmitate
Phenyl dodecanoate	
Phenyl octanoate (weak)	Phenyl hexanoate
Benzyl dodecanoate	
Benzyl decanoate	Benzyl octanoate
*cyclo*Hexyl dodecanoate	*cyclo*Hexyl octanoate
	*cyclo*Hexyl decanoate
Dodecyl phenylacetate	
Decyl phenylacetate	
Oleyl alcohol	
Dibromo-oleyl alcohol	
	Geraniol
Geranyl dodecanoate	Geranyl octanoate
Citronellyl octanoate	Citronellol
	Citronellyl butyrate
3-Methylbutyl octanoate	3-Methylbutanol
3-Methylbutyl hexanoate	3-Methylbutyl propionate
2-Methylbutyl dodecanoate	2-Methylbutyl propionate
2-Methylbutyl decanoate	2-Methylbutyl octanoate
2-Ethylbutyl dodecanoate	2-Ethylbutanol
2-Ethylbutyl decanoate	2-Ethylbutyl octanoate
2-Ethylhexyl dodecanoate	2-Ethylhexyl hexanoate
2-Ethylhexyl octanoate	
	1-Methylheptyl acetate
1-Methylheptyl butyrate	1-Methylheptyl propionate
β-Naphthyl palmitate	3 : 9-Diethyltridecan-6-ol
Quinol dihexanoate	3 : 9-Diethyl-6-tridecyl propionate
Quinol dibutyrate	3 : 9-Diethyl-6-tridecyl nonanoate

W. Schlenk was unable to obtain an addition product from a hydrocarbon $C_{55}H_{112}$, obtained from montanic acid, and this led him to suppose that there might be an upper limit to the length of the chain that can give an adduct. However, if there is an upper limit it seems unlikely that it will be as low as this because octadecyl palmitate (chain length 35 atoms) and dioctadecyl sebacate (chain length 48 atoms) give complexes without difficulty. Moreover, Zimmerschied *et al.* had no difficulty in preparing an adduct from a hydrocarbon fraction containing an average of fifty carbon atoms per molecule.

The behaviour of esters may be summarised as follows: (i) All normal esters containing chains of 9—48 atoms give addition products with urea. (ii) For each side-chain methyl (or ethyl) group on the same side of the saturated main chain as the carbonyl oxygen atom a straight chain of at least 8 atoms * is required to enable the substance to form a complex. If substitution occurs on opposite sides of the molecule, at least 11 atoms * per side-group are required. (iii) A main-chain phenyl group on the same side as the carbonyl-oxygen atom required a straight chain of 9 atoms, whereas the slightly larger *cyclo*hexyl group requires 13 atoms, to enable it to form a complex. (iv) Benzoates do not form complexes. (v) Two short chains are as effective as one long one.

There is only one exception to these rules amongst the 16 non-linear esters examined by previous authors: from 2-ethylhexyl myristate Zimmerschied *et al.* were unable to obtain an adduct. Tested by the method described below, however, lower homologues (octanoate and dodecanoate) gave complexes without difficulty.

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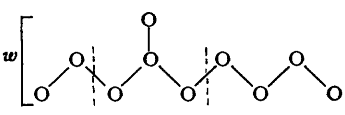
* Measurement of the length of straight-chain does not include the atoms at the widest point of the molecule. Thus, the width is *w* as shown annexed, and the chain-length 6 (not 9). This allows direct comparison of aromatic with aliphatic esters.



EXPERIMENTAL.

Test for Complex Formation.—Urea (3 g.) was moistened with methanol (0·5 ml.), and 50 ml. of a 1% solution of the ester in benzene were added. Next morning the solids were filtered off, washed with benzene (3 × 20 ml.), and dried at room temperature. A positive result for complex formation was indicated by the appearance of an oil or a finely divided solid when the complex was dissolved in water.

Quantitative Separation of Esters.—The method used was very similar to that described by Linstead and Whalley (*loc. cit.*). A mixture of the two esters (2 g. each) was dissolved in light petroleum (100 ml., b. p. 40—60°) and added to urea (10 g.) moistened with methanol (2 ml.). Next morning the solids were filtered off, washed with light petroleum (b. p. 40—60°; 3 × 30 ml.), decomposed with water (100 ml.), and extracted with ether (3 × 100 ml.). The ethereal solution was washed with water (3 × 100 ml.) and dried (Na_2SO_4), and the complex-forming component obtained by distillation of the solvent. The filtrate was washed with water, dried, and evaporated to give the other compound. The following results were obtained (data are for crude materials as obtained from the separations):

(i) *n*-Octadecyl acetate (m. p. 32°; negative Liebermann–Burchardt test) was separated from cholesteryl acetate (m. p. 111°) in 94 and 95% yield respectively; starting materials had m. p. 32° and 113°.

(ii) Octadecyl palmitate (m. p. 57°; negative Liebermann–Burchardt test) was separated from cholesteryl octanoate, m. p. 102°, in 94 and 98% yield respectively. Starting materials had m. p. 57° and 104°.

(iii) Octadecyl palmitate (m. p. 57°; trace of colour in the Liebermann–Burchardt test) was separated from cholesteryl palmitate (m. p. 78°) in 97 and 94% yield respectively. Starting materials had m. p. 57° and 78°.

(iv) Octadecyl acetate (m. p. 31°) was separated from lanosteryl acetate to give 29% of octadecyl acetate and a mixture in the uncombined fraction.

Separation of Octadecyl Dodecanoate from Octadecyl Palmitate.—Equal quantities (2 g.) of the two esters, dissolved in light petroleum (100 ml.), were added to urea (6 g.) moistened with methanol (1 ml.). Next morning the two fractions were isolated as described above. Each fraction was again treated with urea (3 g.) and methanol (0·5 ml.). There were obtained fractions: (i), m. p. 52—55·5°, sap. val. 114 (octadecyl palmitate has m. p. 57° and sap. val. 110·5); and (iv), m. p. 40—43°, sap. val. 122·5 (octadecyl dodecanoate has m. p. 42° and sap. val. 124·5). The saponification values indicate that fraction (i) contained about 75% of palmitate, and fraction (iv) about 86% of dodecanoate.

Separation of the Optically Active Constituent from Commercial Amyl Alcohol.—The alcohol mixture (as used for testing of milk) was converted into the octanoates by treatment with octanoyl chloride, $[\alpha]_D^{18}$ +0·54°. The esters (40 g.), dissolved in light petroleum (200 ml.), were treated overnight with urea (100 g.) and methanol (30 ml.) and worked up in the usual manner. Fraction (1) (13·5 g.) did not combine with urea and had $[\alpha]_D^{18}$ +0·71°; fraction (2) had $[\alpha]_D^{18}$ +0·35°. Fraction (1) was again treated with urea (35 g.) and methanol (10 ml.) to give fraction (3) (uncombined; 6·5 g.), $[\alpha]_D^{18}$ +1·06°. Fraction (3) was treated with urea (6 g.) and methanol (1 ml.), to give fraction (4) (uncombined; 4·5 g.), $[\alpha]_D^{18}$ +1·19°.

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