GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS.

Part VI. The Behaviour of the Acids Derived from 4-Methylcoumarins.

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Though some work has been carried out regarding the influence of alkyl substituents on the behaviour of coumarins towards alkali, it does not seem to be adequate and the results are not very definite. Methyl groups present in the benzene ring, do not markedly affect the properties of the compounds since they exhibit the normal coumarin behaviour by dissolving in alkali to give almost colourless solutions which subsequently become yellow and later on develop a beautiful yellowish green fluorescence, which is taken as an indication of the formation of the coumaric acid. Alkyl groups present in the pyrone ring inhibit these colour effects. According to the observations of Hjelt[1] and Fries and his co-workers,[2] if alkyl groups should be present in the 3- and 4-positions, the opening of the lactone ring takes place more slowly and the corresponding coumarinic acids pass back into the coumarins more easily and quickly.

For the change of the coumarinic acids into the corresponding coumaric acids, the situation seems to be different. With aqueous alkali ordinary coumarinic acid and those containing alkyl groups in the benzene ring go into the coumaric acids only very slowly. With 4-methylcoumarin the change is said to be quicker whereas with 3 : 4-dialkylcoumarins, under similar conditions, no coumaric acid is said to be produced. As for the reverse change Fries and Klostermann[2] found that β : 4-dimethyl and β : 5-dimethylcoumaric acids in glacial acetic acid solution, when treated with concentrated hydrochloric acid at the ordinary temperature changed completely in a few hours to the corresponding dimethylcoumarins. Coumaric and 4-methylcoumaric acids, on the other hand, remained unchanged even after a day. Similar differences were noted even when sulphuric acid was employed.

Dey and his co-workers[3] have isolated a number of fairly stable acids from 4-methyl-β-naphthopyrone and its derivatives by the action of alcoholic

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potash and have attributed the *cis*-configuration to them for the following reasons: (1) The acids could be easily reconverted into the original pyrones, the change being brought about by simply passing dry hydrogen chloride through their suspension in acetic acid or by dissolving in concentrated sulphuric acid and pouring the solution into water. (2) They eliminate water at their melting points and are transformed into the corresponding coumarins. (3) The 3-chloro and bromoderivatives undergo change with alcoholic potash only slowly to give furan carboxylic acids.

Though they believe these properties to be peculiar to 4-methyl-β-naphthopyrone derivatives, a comparison with the acids derived from 4-methyl and 4 : 7-dimethylcoumarins seems to indicate that these are more or less general for all coumarins containing a methyl group in the 4-position. The question seems to be open as to whether they are *cis* or *trans* acids. Fries *et al.* considered the acids they obtained from 4-methyl and 4 : 7-dimethylcoumarins as *trans* acids which possess the peculiar property of closing up the ring easily, whereas Dey and his co-workers considered the acids derived from 4-methyl-β-naphthopyrone as *cis*-acids with remarkable stability. No unequivocal evidence seems to have yet been given in favour of either.

In one of the previous papers[4] of this series it has been shown that dehydrating agents like concentrated sulphuric acid and fuming hydrochloric acid produce the conversion of the coumaric acids into the coumarins, the yield of the products varying with the nature of the substituents in the acids. The acids derived from 4-alkylcoumarins seem to possess this property in a higher degree. Though normally coumaric acids do not close up the ring on simple heating, they do so in the presence of a little mercury compound.[4] Further the esters of coumaric acids all undergo conversion into the coumarins above their melting points.[5] This property of undergoing ring closure on heating therefore does not definitely indicate that the acids derived from 4-methylcoumarins are *cis*-acids. The third argument of Dey *et al.* is based on the assumption that the formation of furan carboxylic acids from 3-chloro or bromo coumarin by the action of potash involves the elimination of a molecule of hydrogen chloride or bromide as such and necessitates the existence of the two atoms concerned in close proximity. According to them, since the acid derived from 4-methyl-3-halogeno-β-naphthopyrone is *cis*, these two atoms are apart and hence their elimination is difficult. There seems to exist no support for this explanation. It is well recognised that elimination of halogens and hydrogen halides takes place more easily from the *trans* positions than from the *cis* and that several transformations such as the Beckmann's transformation involve *trans* positions. The action of potash on 3-bromo-4-methyl-β-naphthopyrone obviously proceeds through the

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initial replacement of the halogen with a hydroxyl group and the subsequent elimination of water.
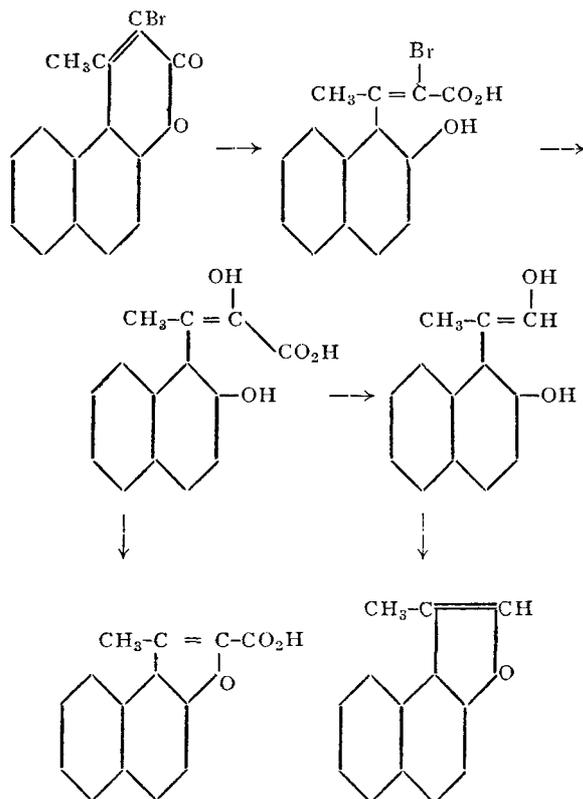
The isolation by Dey and Lakshminarayanan of the aldehyde[3] as a by-product supports this view clearly. Normally the hydroxy acid is stable and undergoes ring closure to the coumarilic acid whereas in the present case it partly undergoes decarboxylation to yield the aldehyde which undergoes further change into the furan only with difficulty. The arguments, therefore, in favour of *cis*-configurations for the acids are not decisive.

On the other hand, there is room for doubt if they are really *cis* acids. They are too stable to be *cis* and further they have not been converted into the *trans*, though ordinarily *cis* acids are readily converted into the stabler *trans* forms by well-known methods. The claim of Dey and Lakshminarayanan[3] to have isolated a second acid (*trans*) from 4-methyl-β-naphtho-pyrone does not seem to be correct. The new acid melts lower than the original '*cis*' acid and undergoes conversion into the pyrone much more readily. On examining this product carefully it is now found that it is a partially mercurated variety of the original acid and hence it melts lower and
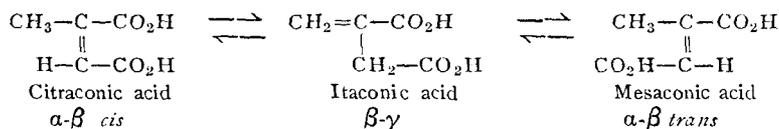
reacts more vigorously. The property of getting transformed into the pyrone by the action of ultra-voilet light or sunlight is possessed by the mercury-free acid melting at the higher temperature in a marked degree.

In view of the indefinite position outlined above, a detailed study of the coumarins containing a methyl group in the 4-position has been made with reference to their conversion into the corresponding *cis* and *trans* acids by the action of alkali. The following pyrones have been examined : (1) 4-methyl-β-naphthopyrone, (2) 4-methyl-α-naphthopyrone, (3) 4-methyl-7-hydroxycoumarin, (4) 4-methyl-7-methoxycoumarin and (5) 4 : 7-dimethyl-coumarin. Amongst these the first undergoes the change into β-2-hydroxy-1-naphthylcrotonic acid very readily. Simple solution in cold alcoholic potash or hot aqueous potash and subsequent acidification is enough to produce the acid. Further boiling effects no further change. Mercuric oxide in the presence of sodium hydroxide produces mercuration of the acid very solwly. Otherwise it effects no isomeric change. The other pyrones in the list dissolve in alkali on simple treatment obviously to produce *cis* acids which get reconverted into the pyrones completely on acidification. Longer boiling with alkali or the use of catalysts like mercuric oxide produce acids which are fairly stable. Some of them can be crystallised from boiling alcohol. All these acids have the common property of undergoing easy conversion into the corresponding pyrones on being subjected to the action of heat or to the action of dehydrating agents. They do not undergo further transformations into stabler acids by continued boiling with aqueous alkali containing mercuric oxide. Under these conditions all known *cis* acids easily get converted into the *trans* compounds. It, therefore, seems to be incorrect to call them *cis* acids. They are really *trans* acids which have the characteristic of easy formation from the pyrones and easy conversion back into them.

In further support of this view the methyl ethers of these compounds have been investigated in detail. The acids undergo methylation easily with dimethyl sulphate in alkaline solution to yield stable ethers. The same compounds are readily obtained from the pyrones by the action of dimethyl sulphate in the presence of aqueous alcoholic potash. Though easily formed, they are really *trans* ethers since they are markedly stable and do not undergo conversion into isomeric compounds by long treatment with acids or mercury compounds.[6] Hence the conclusion is drawn that these ethers and the corresponding hydroxy acids belong to the *trans* group.

The remarkable ease with which these *trans* acids are produced from the 4-methyl pyrones and the readiness with which they undergo conversion into the pyrones can be easily explained when it is realised that just as

in the case of citraconic and mesaconic acids, a facile tautomeric mechanism for interconversion exists in them. Linstead and Mann[7] have shown that with citraconic and mesaconic acids the configurational change in the α-β acids proceeds entirely through the intermediate formation and decomposition of the β-γ isomeride as follows :—

$$CH_3-C-CO_2H \quad \rightleftarrows \quad CH_2=C-CO_2H \quad \rightleftarrows \quad CH_3-C-CO_2H$$
$$\overset{\|}{H-C-CO_2H} \qquad\qquad \overset{|}{CH_2-CO_2H} \qquad\qquad \overset{\|}{CO_2H-C-H}$$

Citraconic acid   Itaconic acid   Mesaconic acid
α-β *cis* β-γ α-β *trans*

The velocity of the stereochemical change is rather high. This is also supported by the observation of Fittig and Kettner[8] in regard to dimethylmaleic and fumaric acids. Further it is a characteristic of this mechanism that it enables the *trans* to *cis* change to take place with ease. The following represents the change in the case of 4-methylcoumarins.

α-β *cis* β-γ

α-β *trans*
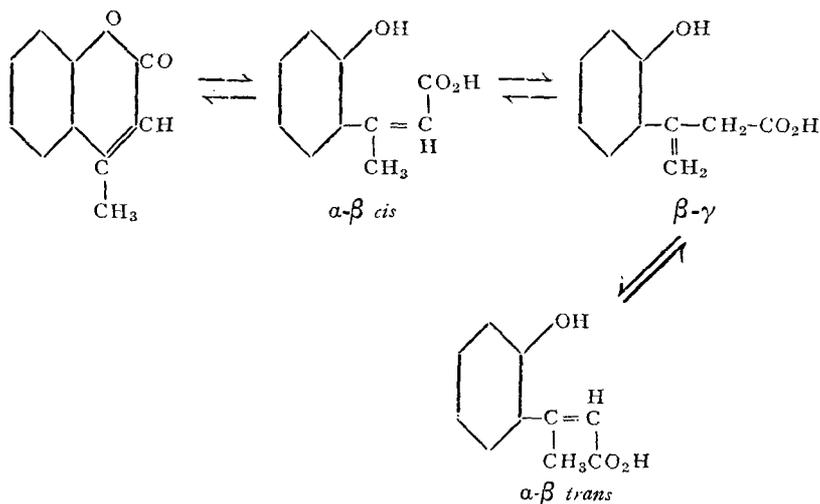
The tautomeric mechanism is not found to take place in aliphatic monocarboxylic acids. But in the case of the methylcoumarinic and coumaric acids the phenyl ring obviously performs the same function as the second carboxyl in citraconic and mesaconic acids. In this connection the similarity that exists between malonic and phenylacetic acids in possessing the reactive methylene group may be mentioned.

Regarding the effect of the methyl group in position 4, all observations indicate that *cis* acids cannot be isolated since they are very unstable and go over into the pyrones on the one hand or into the *trans* acids on the other very readily. The *trans* acids that are easily formed are not however very stable. Though unaffected by alkali they get converted into the coumarins

on being subjected to heat or dehydrating agents or acids. They form, therefore, a remarkable series of unstable *trans* acids.

<center>*Experimental.*</center>

Preparation of the 4-methylcoumarins.—Equimolecular quantities of the appropriate phenolic compound and ethyl aceto acetate were condensed in the presence of concentrated sulphuric acid. 4-methyl-*a*-naphthopyrone, 4-methylumbelliferone and 4 : 7-dimethylcoumarin were obtained very readily by the methods found in the literature. 4-methyl-*β*-naphthopyrone was produced in a rather poor yield by the method of Dey and Lakshminarayanan.[9] It has now been found that by reducing the amount of sulphuric acid the process is rendered simpler and the yield improved.

A mixture of finely powdered *β*-naphthol (14 g.) and ethyl aceto-acetate (15 g.) was slowly added to concentrated sulphuric acid (16 c.c.) which was cooled under the tap. After allowing the mixture to stand overnight, it was poured into excess of crushed ice. The solid product was washed with water, subsequently shaken with dilute sodium hydroxide solution and crystallised from ethyl alcohol. It melted at 183°C. and the yield was about 8 grams.

The methylation of 4-methyl-7-hydroxycoumarin using methyl iodide or dimethyl sulphate and sodium hydroxide gave rise only to a poor yield of 4-methyl-7-methoxycoumarin due to the opening up of the pyrone ring and the formation of by-products. The process was therefore conducted in dry acetone medium using methyl iodide and anhydrous potassium carbonate. 4-Methyl-7-hydroxycoumarin (4 g.) was dissolved in dry acetone (100 c.c.), methyl iodide (7 c.c.) and anhydrous potassium carbonate (10 g.) added and the contents slowly refluxed on a water-bath for about five hours. The solvent was then distilled off, water added and the mixture stirred well in order to dissolve the alkali carbonate. The insoluble solid was filtered and crystallised from alcohol. It melted at 160° and the yield was 4 grams.

The trans *acids and their reactions.* *β-2-Hydroxy-1-naphthylcrotonic acid.*—This acid was prepared by Dey and Lakshminarayanan by boiling 4-methyl-*β*-naphthopyrone with aqueous alcoholic potash for four hours and the subsequent acidification of the alkaline solution after removing the alcohol. It is now found that the same acid could be obtained by simpler procedure.

(1) *Action of hot aqueous potash.*—The pyrone (2 g.) was dissolved in twenty per cent. aqueous potash (20 c.c.) by boiling for a few minutes, diluted with water to about 100 c.c. and cooled. The clear solution yielded

on acidification an almost theoretical yield of the crotonic acid which was purified by dissolution in sodium bicarbonate and subsequent crystallisation from alcohol.

(2) *Action of cold aqueous alcoholic potash.*—The pyrone (2 g.) was treated with alcohol (30 c.c.) and twenty per cent. aqueous potash (20 c.c.) and shaken. The substance went into solution rapidly. The clear solution was then diluted with water, acidified and the crystalline solid was purified as above. The yield was almost theoretical.

(3) *Action of mercuric oxide and cold alkali.*—The finely powdered pyrone (2 g.) was shaken in the cold for half an hour with aqueous caustic soda (2 g. in 50 c.c.) and yellow mercuric oxide (1 g.). The pyrone rapidly dissolved. After filtering off the mercuric oxide, the filtrate was first treated with hydrogen sulphide in order to remove any combined mercury and finally acidified. The precipitated acid was purified as above.

(4) *Action of mercuric oxide and hot aqueous alkali.*—Following the procedure of Dey and Lakshminarayanan,[3] a substance decomposing at about 112° was obtained. It however contained mercury (about five per cent.). It was therefore dissolved in caustic alkali and the mercury removed by passing hydrogen sulphide. After filtering off the mercuric sulphide, the clear filtrate on acidification gave the acid melting at 148° and found to be identical with the samples obtained by other methods. It was therefore concluded that the substance decomposing at 112° was a mixture of the acid with some mercurated sample of it.

The pure acid decomposes at 148° and crystallises from alcohol as colourless plates tapering at the ends. It is sparingly soluble in cold water and is more soluble in hot water. In acid medium it gets converted into the pyrones in the course of 24 hours. It is quite stable in alkali. The action of mercuric oxide in the cold or hot alkaline solution or of mercuric acetate in neutral solution produced no change except partial mercuration and when the combined mercury was removed with hydrogen sulphide, the original acid was recovered unchanged.

At the melting point, the acid evolves water and gets completely converted into pyrone. One gram of the acid in 25 c.c. of alcohol was exposed in a silica flask to sunlight. After about 8 hours the sparingly soluble pyrone began to crystallise out and after 24 hours exposure, the solvent was distilled off and the residue was found to be the pure pyrone melting at 183°. There remained no detectable amount of the original acid. Quite a similar behaviour was noted in the presence of ultra-voilet light, complete conversion taking place within 24 hours. Under the conditions described by Dey and

Lakshminarayanan[3] using chloroform as solvent, bromine as catalyst and ultra-voilet light as the source of energy, 60 per cent. of the acid melting at 148° underwent conversion into the pyrone whereas the impure acid melting at 112° changed almost completely into the pyrone, though the product had to be crystallised repeatedly before it could give the correct melting point of 4-methyl-β-naphthopyrone.

*4-Hydroxy-β-methylcoumaric acid or β-2 : 4-dihydroxyphenylcrotonic acid.—*4-Methyl-7-hydroxycoumarin (2 g.) was dissolved in about 50 c.c. of 0·5 per cent. aqueous sodium hydroxide and the cold solution shaken with yellow mercuric oxide (2 g.) for about an hour. Mercuration took place consuming a good amount of the mercuric oxide. The remaining oxide was filtered off and the filtrate treated with hydrogen sulphide in order to remove all combined mercury as sulphide. After filtering off the sulphide, the clear solution was acidified at 0°. The precipitated acid was purified by dissolving in aqueous sodium bicarbonate and reprecipitating at the temperature of melting ice. It sintered strongly at about 115° and melted at 185°. It could not be crystallised from boiling alcohol as it rapidly underwent change into the original pyrone. The solution of the acid in sodium bicarbonate or in sodium hydroxide gave a blue fluorescence.

*4-Methoxy-β-methylcoumaric acid or β-2-hydroxy-4-methoxyphenylcrotonic acid.—*This was prepared from 4-methyl-7-methoxycoumarin using alkali and mercuric oxide. About 2 g. of the coumarin · were dissolved in hot 20 per cent. potassium hydroxide (30 c.c.). The solution was diluted to 100 c.c. with water, cooled and shaken with yellow mercuric oxide (2 g.) for about an hour. It was filtered, the filtrate treated with hydrogen sulphide in order to remove all combined mercury as mercuric sulphide and finally acidified. It was first purified by solution in sodium carbonate and reprecipitation and subsequently crystallised from aqueous alcohol. It was obtained as colourless rectangular plates melting at 145° with decomposition. [Found : C, 63·2 per cent.; H, 6·0 per cent. ; $C_{11}H_{12}O_4$ requires C, 63·5 per cent. ; H, 5·8 per cent.] The acid undergoes conversion into the coumarin with great ease on heating to its melting point and in the presence of concentrated hydrochloric and sulphuric acids in the cold. It is unaffected by prolonged reaction with alkali and mercuric oxide. It undergoes condensation with mercuric acetate rather readily but the product yields only the original acid on being decomposed with hydrogen sulphide.

*β : 4-Dimethylcoumaric acid or β-2-hydroxy-4-methylphenylcrotonic acid.—*4 : 7-Dimethylcoumarin undergoes conversion in boiling aqueous potash only very slowly. The acid could, however, readily be obtained by shaking with

alkali and mercuric oxide exactly as mentioned for 4-methyl-7-methoxy coumarin. It crystallised from dilute alcohol in the form of stout needles melting at 157° with decomposition (compare Fries and Klostermann[2]—142° decomp. and Perci[10]—136° decomp.). [Found C, 68·6 per cent. ; H, 6·2 per cent. ; $C_{11}H_{12}O_3$ requires C, 68·8 per cent. ; H, 6·3 per cent.] It is sparingly soluble in water and readily in alcohol. It is also soluble in ether and acetone but not in chloroform, carbon disulphide or benzene. It is fairly stable in the presence of dilute alkali and dilute acid but with concentrated acids in the cold it undergoes conversion into the coumarin.

A sample of the acid was decomposed at its melting point (heating for about fifteen minutes at 160°). Though the product was completely insoluble in sodium bicarbonate and was therefore free from the original acid, it could not be easily crystallised from alcohol. One per cent. aqueous sodium hydroxide removed a small quantity of the impurity and the residue was found to be the pure pyrone which could now be easily crystallised. The alkali solution yielded on acidification a very small quantity of a substance giving a brown colour with ferric chloride. This was probably an indication that small quantities of the corresponding hydroxy-styrene are also formed.

When exposed to sunlight or ultra-voilet light in absolute alcoholic solution for twenty-four hours, it underwent complete conversion into the coumarin. On the other hand, mercury compounds in alkaline medium produced no change.

Preparation and properties of the ethers of the acids. β-*2-Methoxy-1-naphthylcrotonic acid.*—The hydroxy acid was dissolved in excess of dilute aqueous potash and methylated by shaking with excess of dimethyl sulphate in the cold for one hour. The excess of dimethyl sulphate was decomposed by heating for a short period at 100° and the methoxy acid finally liberated by acidification. It was repeatedly crystallised from dilute alcohol when it was obtained as colourless needles melting at 190°. [Found : C, 74·1 ; H, 5·9 per cent. ; equivalent weight 242·9 ; $C_{15}H_{14}O_3$ requires C, 74·4 and H, 5·8 per cent.; equivalent weight 242·0.]

The same ether was obtained from the pyrone by the action of sodium methoxide and methyl iodide according to the method of Reychler.[11] But the yield and purity of the product were not good. However, it was more readily obtained from the pyrone by methylation with dimethyl sulphate and potash using aqueous methyl alcoholic medium. 4-Methyl-β-naphthopyrone (6 g.) was dissolved in a boiling mixture of methyl alcohol (50 c.c.) and 20 per cent. aqueous sodium hydroxide (50 c.c.). After cooling it to 50° the solution

was agitated with dimethyl sulphate (30 g.) which was slowly added in the course of half an hour. The reaction mixture was then made sufficiently alkaline, some more methyl iodide added and the whole boiled under reflux on a water-bath for three hours. The alcohol was then distilled off and the contents were diluted and acidified. The product was purified by solution in sodium bicarbonate and reprecipitation and crystallisation from dilute alcohol.

The methyl ether was unaffected by prolonged heating at its melting point. After treatment with mercuric oxide in both cold and hot alkaline solution it was recovered unchanged. Mercuric chloride in alcoholic or aqueous solution produced no change when boiled with the substance for two to three hours. After the heating was over, most of the alcohol was distilled off, a few drops of concentrated hydrochloric aicd added along with a large volume of water and the mixture allowed to cool. The original ether was recovered unchanged. A similar result was obtained by the action of mercuric acetate in neutral or faintly acid medium.

The methoxy acid was dissolved in anhydrous ethyl alcohol saturated with hydrogen chloride in the cold, allowed to stand for 24 hours and boiled under reflux for two hours. The alcohol was then distilled off, the residue treated with water and ether extracted. The oily liquid that was obtained from the ether solution on evaporation was hydrolysed with dilute alkali and the resulting acid isolated. It was identical with the original acid. The oil obtained during the course of the experiment was the ester of this acid.

β-1-Methoxy-2-naphthylcrotonic acid.—β-1-Hydroxy-2-naphthylcrotonic acid could not be obtained pure from 4-methyl-α-naphthopyrone. Though it was formed easily it underwent reversion into the pyrone readily on acidifying the alkaline solutions and the pyrone invariably contaminated it. The methoxy compound was, however, easily obtained by methylation of the pyrone with dimethyl sulphate in aqueous alcoholic potash. After three crystallisations from dilute alcohol it was obtained as colourless rectangular plates melting at 140°. [Found: C, 74·3 per cent.; H, 5·3 per cent.; $C_{15}H_{14}O_3$ requires C, 74·4 per cent.; H, 5·8 per cent.]

The substance melted without decomposition. The action of mercuric compounds and alcoholic hydrogen chloride was studied carefully and they were found to produce no change, thus showing that it is not a *cis* compound.

β-2 : 4-Dimethoxyphenylcrotonic acid or methylether of 4-methoxy-β-methyl coumaric acid.—This was obtained from a number of starting materials using suitable methods as given below :—

(1) From β-2 : 4-dihydroxyphenylcrotonic acid (β-methylumbellic acid) by methylation with dimethyl sulphate in aqueous alkaline solution.

(2) From β-2-hydroxy-4-methoxyphenylcrotonic acid (β-methylumbellic acid methylether) by the same method.

(3) From 4-methyl-7-hydroxycoumarin by methylation with dimethyl sulphate in aqueous alcoholic solution.

(4) From 4-methyl-7-methoxycoumarin by using the same method.

All the samples were found to be identical. The substance crystallised from dilute alcohol as colourless needles melting at 150°. [Found : C, 65·0 ; H, 6·1 per cent. ; $C_{12}H_{14}O_4$ requires C, 64·9 ; H, 6·3 per cent.] This methoxy acid also melted without decomposition and was unaffected by all the reagents which produce *cis* to *trans* inversion.

β-2-Methoxy-4-methylphenylcrotonic acid or β-4-dimethylcoumaric acid methyl ether.—β : 4-Dimethylcoumaric acid was methylated using dimethyl sulphate and potash in aqueous solution. The ether so obtained crystallised from aqueous alcohol in the form of fibrous needles melting at 125-26°. [Found : C, 69·9 ; H, 7·0 ; OCH$_3$, 14·7 per cent. ; $C_{12}H_{14}O_3$ requires C, 69·9 ; H, 6·8 and OCH$_3$, 15·0 per cent.]

This substance exhibited the same behaviour as the other ethers described before and remained unchanged under conditions which bring about *cis* to *trans* inversion.

Summary.

The action of alkali on a number of coumarins with methyl groups in the 4-position has been studied in detail. Each of them yields readily only one acid which, though fairly stable, has the property of undergoing change into the corresponding coumarin under the action of heat and dehydrating agents. The acids, however, cannot be converted into stabler isomers by methods which are definitely effective in converting *cis* into *trans* acids. The methyl ethers of the acids are easily obtained by methylating the acids or the original pyrones in the presence of alkali in an aqueous alcoholic medium. Their properties are those of ethers of the *trans* acids since they cannot be converted into isomeric compounds by methods which are definitely successful in converting *cis* into *trans* ethers. It is therefore concluded that the acids and their ethers derived from 4-methylcoumarins are *trans* compounds. The comparatively ready formation of these acids and their ready conversion again into the coumarins are explained on the basis of the tautomeric mechanism which renders the geometrical inversion very facile.

REFERENCES.

1. Hjelt, *Ber.*, 1894, **27**, 3332.

2. Fries and Volk, *Ann.*, 1911, **379**, 92.
   Fries and Klostermann, *Ber.*, 1906, **39**, 871.
   „   „   *Ann.*, 1908, **362**, 2 and 28.

3. Dey, *J.C.S.*, 1915, **107**, 1606.
   Dey, Row and Sankaranarayanan, *J.I.C.S.*, 1932, **9**, 281.
   Dey and Lakshminarayanan, *ibid.*, 1934, **11**, 373.

4. Seshadri and Suryaprakasa Rao, *Proc. Ind. Acad. Sci.*, (A), 1936, **4**, 157.

5. Dey, Rao and Seshadri, *J.I.C.S.*, 1934, **11**, 743.

6. Rangaswami and Seshadri, *Proc. Ind. Acad. Sci.*, (A), 1937, **5**, 249.

7. Linstead and Mann, *J.C.S.*, 1931, 726.

8. Fittig and Kettner, *Ann.*, 1898, **304**, 156.

9. Dey and Lakshminarayanan, *J.I.C.S.*, 1932, **9**, 149.

10. Perci, *Die Coumarine*, by Simonis, p. 117.

11. Reychler, *ibid.*, by Simonis, p. 87.