The Stability of Coumarinic Acids Derived from βα-1 :2-Naphthapyrones.

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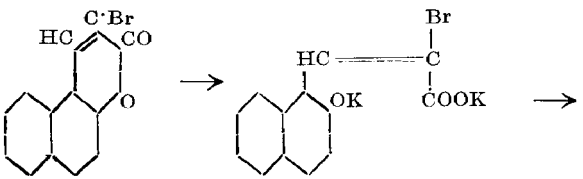
Although coumarinic or *cis-ortho*-hydroxycinnamic acids, as a class, are unstable, and are reconverted into coumarins when a solution of their alkali salts is acidified, there are a few exceptions recorded in literature of moderately stable coumarinic acids such as those derived from 8-nitrocoumarin (Miller and Kinkelin, *Ber.*, 1889, **22**, 1706), 3-acetyl-4 : 5 : 7-trimethylcoumarin-6 : 8-dicarboxylic acid diethyl ester (Jordan and Thorpe, *J. Chem. Soc.*, 1915, **107**, 387), 6-nitro-αβ-1 : 2-naphthapyrone and 6-nitro-αβ-1 : 2-naphthapyrone-4-acetic acid (Dey, *J. Chem. Soc.*, 1915, **107**, 1606), and a few others. It will be noticed that in all these cases the coumarinic acid is stabilised by the entrance of acidic groups, *e.g.*, nitro or carboxyl, the effect being most marked when the acid radicle is in position-8. Thus the separation of a mixture of 6-nitro-and 8-nitrocoumarins has been made by taking advantage of the superior stability of the coumarinic acid derived from the latter (Dey and Krishnamurthi, *J. Indian Chem. Soc.*, 1927, **4**, 197). The entrance of alkyl groups, on the other hand, either in the benzene or in the pyrone rings, is found to produce the opposite effect (*cf.* Hjelt, *Ber.*, 1894, **27**, 3332 ; Fries and Volk, *Annalen*, 1911, **379**, 92).

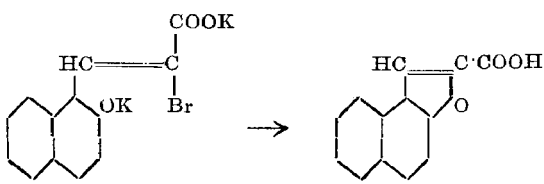
Certain βα-1 : 2-naphthapyrone derivatives, *e.g.*, 4-methyl-βα-1 : 2-naphthapyrone, 3-chloro-4-methyl-βα-1 : 2-naphthapyrone and βα-1 : 2-napthapyrone-4-acetic acid (Dey, *J. Chem. Soc.*, 1915, **107**, 1618) appear, therefore, to be quite exceptional in as such as they provide the only known examples of coumarins yielding stable coumarinic acids notwithstanding the presence of alkyl groups and the absence of any acidic substituents in the ring. The anomaly becomes most striking when the behaviour of these is compared with that of the isomeric αβ-1 : 2-naphthapyrones having alkyl substituents in similar positions in the ring. The latter give only unstable *cis*-acids which undergo ring-closure, the moment they are liberated from their alkali salts.

The production of these stable coumarinic acids was considered at first to be characteristic of all $\beta\alpha$-naphthapyrones, but a study of this reaction with different members of the $\beta\alpha$-naphthapyrone series has now shown that the stability of the *cis*-acids is apparently connected with the presence of an alkyl group in position-4 in the pyrone ring. This fact was brought into prominence while the action of alkalis on 3-bromo $\beta\alpha$-1 : 2-naphthapyrone (I) and 3-chloro-4-methyl-$\beta\alpha$-1 : 2-naphthapyrone (II) respectively was being investigated. They exhibited a curious difference : the former reacted normally like other 3-halogen substituted coumarins, and yielded the usual furan derivative (III) with the elimination of alkali bromide, while the latter was converted into the remarkably stable chloro-$\beta\alpha$-naphthacoumarinic acid (IV) from which no elimination of alkali chloride was possible under the usual conditions.



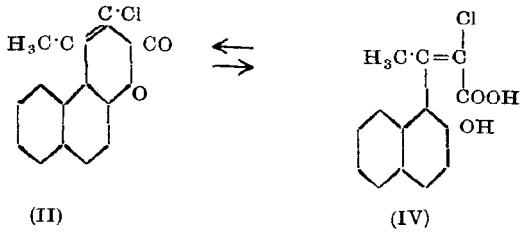
(I)

cis-α-Bromo-β-2-hydroxy-1-naphthylacrylic acid (K-salt) (unstable).



(III)

trans-Acid. β-Naphthafurancarboxylic acid.

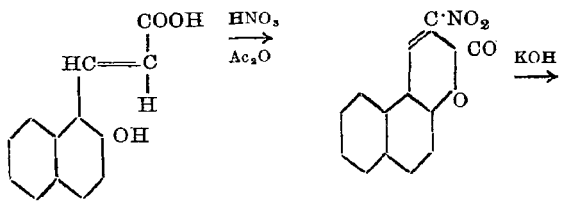


(II) (IV)

cis-α-Chloro-β-2-hydroxy-1-naphthylcrotonic acid (stable).

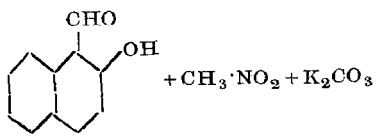
The presence of a CH_3 group in position-4 in the pyrone ring, or its absence, must therefore be regarded as the only factor with which this remarkable difference of behaviour with alkalis is associated.

The reaction of 3-nitro-βα-1:2-naphthapyrone with alkalis is equally interesting. When the stable *trans*-or β-naphthacoumaric acid is carefully nitrated in acetic anhydride solution, a nitro group enter position-3 with the simultaneous closure of the pyrone ring, and when the nitro derivative is treated with hot alkali, the pyrone ring is completely ruptured and 2-naphthol-1-aldehyde obtained in a quantitative yield. The following equations represent the reactions taking place.



trans-β-2-Hydroxy-1 naphthylacrylic acid (stable, m.p. 165°).

3-Nitro-βα-1:2-naphthapyrone (m.p. 244°).



β-Naphthol-α-aldehyde (m.p. 81°).

It is clear, therefore, that the entrance of a nitro group makes the pyrone ring unstable.

The stable β-naphthacoumarinic acids have been assigned the *cis*-configurations on the sole evidence of the extraordinary ease with which they are converted into the original coumarins when (*a*) they are heated to their melting points, (*b*) they are crystallised from hot solvents like acetic acid, or (*c*) they are even preserved in a desiccator for several days (*cf.* Dey, *loc. cit.*). It must be noted, however, that hitherto all attempts to convert these stable *cis*-or coumarinic acids into their *trans*-isomers have been unsuccessful, although the other coumarins which give only unstable *cis*-acids have all been converted by the usual methods into the stable *trans*-or coumaric acids. A comparative study of the stabilities of the coumarinic acids derived from a few representative members of the βα-1:2-naphthapyrone family has now been made, and the results are summarised in the following table.

Name.	M.p.	*cis*-Acid.	*trans*-Acid.
βα-1:2-Naphthapyrone	118°	Unstable.	Stable, colourless needles, m.p. 165°.
4-Methyl-βα-1:2-naphthapyrone	181°	Stable, soft colourless plates with a pearly lustre, m.p. 146° (decomp.).	Not known.
3-Chloro-4-methyl-βα-1:2-naphthpyrone	135°	Stable, colourless mica like plates, m.p. 148° (decomp).	Not known.
?-Nitro-4-methyl-βα-1:2-naphthapyrone	274°	Stable, small yellow prisms, m.p. 271° (decomp.).	Not known.
βα-1:2-Naphthapyrone-4-acetic acid	191°	Stable, pale yellow plates, m.p. 174° (decomp.).	Not known.
βα-1:2-Naphthapyrone-3-acetic acid	265°	Unstable.	Stable, colourless plates, m.p. 79°.
4-Methyl-βα-1:2-naphthapyrone-3-acetic acid	199°	Stable, colourless shining plates, m.p. 154° (decomp.).	Not known.
3-Methyl-βα-1:2-naphthapyrone	158°	Unstable.	Stable, colourless plates, m.p. 138°.
3-Bromo-βα-1:2-naphthapyrone	165°	Unstable.	Not known. Changes into β-naphthafurancarboxylic acid, m.p. 192°.
3-Nitro-βα-1:2-naphthapyrone	244°	Unstable, decomposes into 2-naphthol-1-aldehyde, m.p. 81°	

The following conclusions may legitimately be drawn from the results tabulated above.

(*a*) The unsubstituted $\beta\alpha$-1:2-naphthapyrones or those with a methyl or an acetic acid group in position-3 in the pyrone ring, behave normally and yield only unstable *cis*- or coumarinic acids.

(*b*) $\beta\alpha$-1:2-Naphthapyrones having a methyl- or an acetic acid group in position-4, yield stable coumarinic acids, but the latter cannot be transformed by the usual means into the isomeric *trans*- or coumaric acids. The stability of these *cis*-acids is not influenced in any way by the introduction of another atom or group in position-3.

(*c*) The pyrone ring is rendered unstable by the introduction of negative elements or groups, *e.g.*, Cl, Br, or NO_2 in the 3-position, the latter being removed by boiling alkalis, so long as position-4 is unoccupied.

The work on the influence of substituting groups other than alkyl, *e.g.*, OH, NO_2, COOH, etc., in position-4, on the stability of *cis*-acids derived rrom $\beta\alpha$-1:2-naphthapyrones alone, is in progress.

Experimental.

$\beta\alpha$ 1:2-Naphthapyrone.—This was prepared by modifying the conditions described by Kauffmann (*Ber.*, 1883, **16**, 683). The yield was much improved and less tarry matter was associated with the crude product by heating the mixture in a sealed tube at a lower temperature (160°) for 3—4 hours. The product was washed with 50 p.c. methanol, and the residue crystallised twice from boiling absolute alcohol. A maximum yield of 3·8 g. of the pure pyrone (m.p. 118°) was obtained from 5 g. of the naphthol-aldehyde.

trans-*β-2-Hydroxy-1-naphthylacrylic acid* (*β-Naphthacoumaric acid*).—On boiling the β-naphthapyrone with 2*N*-alkali for several hours and acidifying the clear solution, only unchanged coumarin was precipitated. The pyrone (1 g.) boiled with 40 p.c. caustic potash for 5 hours, gave 0·15 g. of the courmaric acid, m.p. 165° (decomp.), the remainder of the coumarin being recovered unchanged. (Found: Eq. wt., 215. $C_{13}H_{10}O_3$ requires Eq. wt., 214).

cis-*β-2-Hydroxy-1-naphthylcrotonic acid* (*4-Methyl-β-naphthacoumarinic acid*) (Dey, *J. Chem. Soc.*, 1915, **107**, 1630).—The acid crystallised in lustrous plates on acidifying the cooled alkaline

filtrate. It melts sharply at 146° evolving steam and passing over nto the original pyrone (m.p. 180°). (Found: Eq. wt., 229·8. $C_{14}H_{12}O_3$ requires Eq. wt., 228).

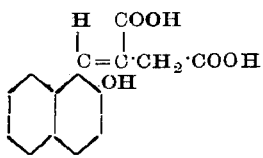
cis-*α-Chloro-β* 2-*hydroxy*-1-*naphthylcrotonic acid* (3-*Chloro*-4-*methyl-β-naphthacoumarinic acid*) (Dey, *loc. cit.*, 1630).—The acid crystallised in the same way as the preceding acid, m.p. 148°, and passed over into the coumarin (m.p. 135°). (Found: Eq. wt., 266. $C_{14}H_{11}O_3Cl$ requires Eq. wt., 262·5).

?-*Nitro*-4 *methyl-β*α-1 : 2-*naphthapyrone*.—4-Methyl-β-naphthacoumarinic acid (1 g.) was suspended in acetic anhydride (10 c.c.) and the ice cold mixture treated with the calculated quantity of fuming nitric acid (0·25 c.c.). The solid dissolved immediately and from the clear orange solution, a crystalline solid slowly separated out. The solid was collected after 12 hours, and crystallised twice from hot glacial acetic acid in minute yellow needles sintering at 268° and melting at 273°. It is insoluble in cold sodium carbonate or alkalis. Analysis showed it to be a pure mononitro derivative. (Found: N, 5·45. $C_{14}H_9O_4N$ requires N, 5·49 per cent.).

cis-*β*-2-*Hydroxy*-?-*nitro*-1-*naphthylcrotonic acid*.—The clear orange-red solution by boiling the preceding nitro body with 2*N*-alkali precipitated the acid as a yellow amorphous solid on acidification. It dissolved in cold sodium bicarbonate and was converted at its melting point (271°) into the original pyrone (m.p. 273°). Analysis gave values agreeing with those required for the free acid formed by rupturing the pyrone ring. (Found: N, 5·2. $C_{14}H_{11}O_5N$ requires N, 5·08 per cent.).

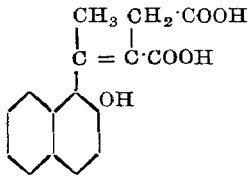
cis-*β*-2-*Hydroxy*-1-*naphthylglutaconic acid* (Dey, *loc. cit.*).—It was prepared from β-naphthapyrone-4 acetic acid as a yellow crystalline powder (m.p. 174°) decomposing at its melting point into the pyrone (m. p. 191°) and water vapour in the manner characteristic of coumarinic acids. The pyrone-acetic acid then loses carbon dioxide and forms ultimately the 4-methyl-β-naphthapyrone (m. p. 180°).

trans-*β*-2-*Hydroxy*-1-*naphthylitaconic Acid*.



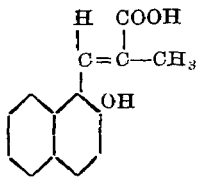
This was prepared from β-naphthapyrone-3 acetic acid (Dey and Sankaranarayan, *J. Indian Chem. Soc.*, 1931, **8**, 817) by the method described by Sen and Chakravarti (*J. Indian Chem. Soc.*, 1930, **7**, 247). The pyrone (1 g.) is dissolved in 5 p.c. caustic soda (20 c.c.), the solution boiled for 10 minutes, diluted to 60 c. c. and red mercuric oxide (1 g.) added. The mixture was boiled under reflux for 1 hour, filtered and acidified when only an opalescent solution was obtained. This was extracted 4 times with ether (80 c. c.) and the ethereal layer separated and re-extracted with a small quantity of 2 *N*-caustic soda (15 c. c.). On acidifying the alkaline extract, the acid came down in tiny plates, m. p. 75-76°. Crystallisation from the minimum amount of hot glacial acetic acid gave colourless rectangular plates, m. p. 79°. (Found: Eq. wt., 142. $(C_{15}H_{12}O_5)\frac{1}{2}$ requires Eq. wt., 136).

cis-*ββ-Methyl-2-hydroxy-1-naphthylitaconic Acid.*



This was prepared from 4-methyl-β-naphthapyrone-3-acetic acid (Dey and Sankaranarayan, *loc. cit.*) by dissolving in 2*N*-caustic soda at room temperature and acidifying the solution after 1 hour. It crystallised in colourless shining plates, m. p. 154° and changing immediately with separation of water into the pyrone-3 acetic acid (m. p 199°). (Found: Eq. wt., 144. $(C_{16}H_{14}O_5)\frac{1}{2}$ requires Eq. wt., 143).

trans-β-2-*Hydroxy-1-naphthylmethacrylic Acid.*



When 3-methyl-β-naphthapyrone (Bartsch, *Ber.*, 1903, **36**, 1970) was boiled with 40 p.c. caustic soda for 2 hours and the clear solution acidified, only the unchanged material (m.p. 158°) was precipitated. The *trans* or coumaric acid was obtained only through the agency of mercuric oxide by the process described before. It was thrown down from the alkaline filtrate as a white precipitate which crystallised from boiling dilute acetic acid as colourless plates, m. p. 138°. (Found: Eq. wt., 228. $C_{14}H_{12}O_3$ requires Eq. wt., 228).

The *methyl ester*, prepared in the usual way, crystallised from methanol in clusters of colourless plates, m. p. 130°. It is insoluble in alkali carbonate but dissolves in caustic soda with a pale yellow colour.

3-*Bromo*-$\beta\alpha$-1 : 2 *naphthapyrone*.—β-Naphthapyrone (2 g.), dissolved in carbon disulphide (5 c. c.) was treated with a solution of bromine (1·6 g.) in the same solvent (5 c. c.) and the mixture exposed in a silica flask to bright sunlight for 6 hours. The colour darkens on exposure. The solvent was evaporated off at ordinary temperature when a dark red mass presumably containing the dibromide was left as residue. It smelt strongly of bromine and was sparingly soluble in alcohol, but all efforts at getting it in a pure crystalline condition were fruitless. The mass (2·3 g) was suspended in methanol, treated with 2*N*-caustic soda (5 c. c.) and the mixture heated on a boiling water-bath for $\frac{1}{2}$ hour The resulting solid crystallised from dilute alcohol in white silky needles, m.p. 165° (decomp.), yield 0·6 g. (Found: Br (by Stepanow's method), 29·26. $C_{13}H_7O_2Br$ requires Br, 29·06 per cent.).

β Naphthafurancarboxylic acid.—The bromopyrone (0·4 g.), dissolved in alcohol (.0 c. c.) was treated with 30 p. c. caustic potash (5 c. c.) and warmed on the water-bath. The clear solution very soon deposited crystals of the sparingly soluble potassium salt of the furancarboxylic acid. It dissolved on boiling with excess of water and crystallised again in fine yellow needles on cooling the solution. The free acid (m. p. 192°) was obtained by trituration with hot water containing hydrochloric acid. (Found: Eq. wt., 215·3. $C_{13}H_8O_3$ requires Eq. wt., 212).

3-*Nitro*-$\beta\alpha$-1 : 2-*naphthapyrone*.—Direct nitration of the pyrone generally resulted in a mixture from which it was difficult to isolate the pure mononitro derivative. The latter was obtained by nitrating β-naphthacoumaric acid under precisely the same conditions as those employed in nitrating 4-methyl-β-naphthapyrone. It crystallised

from a large volume of hot acetic acid in orange yellow needles, m. p. 244°. (Found: N, 5·85. $C_{13}H_7O_4N$ requires N, 5·81 per cent.).

The position of the nitro group was revealed by the action of hot alkali on the compound. On boiling the nitro body with 30 p. c. caustic potash for a few minutes and acidifying the clear cold solution, a yellow oil separated which, on distilling in steam, passed over and condensed in the receiver as a pale yellow crystalline solid. A single crystallisation from dilute alcohol gave colourless needles melting at 81° not depressed by admixture with 2-naphthol-1-aldehyde. It was also identified by conversion into the phenylhydrazone.

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