[CONTRIBUTION FROM THE INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE]

Studies on the Ultraviolet Absorption Spectra of Coumarins and Chromones.[1] Part I

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Received June 19, 1956

Ultraviolet absorption spectra of several coumarins and chromones and their methyl derivatives measured in the region 220–340 mμ show that it is possible to distinguish between them on the basis of absorption characteristics. A methyl group present either in the benzene or in the pyrone ring fails to show any significant change in the absorption properties of the parent compounds.

Benzo-α-pyrone and benzo-γ-pyrone, known respectively as coumarin and chromone are the parents of a large number of naturally occurring compounds. Methods for the synthesis of chromones *viz.*, the Simonis reaction—condensation of phenols with β-keto-esters in the presence of phosphorus pentoxide and the Kostanecki-Robinson reaction—conversion of *o*-hydroxyaryl ketones to chromones by heating with an acid anhydride and the corresponding sodium salt, sometimes lead to the formation of α-pyrone derivatives.[2,3] It is not always an easy task to distinguish between a coumarin and a chromone. Formation of the 2-styryl derivative has been employed as a means for identification of chromones;[4] but only 2-methylchromones possess this property thus limiting its usefulness. Formation of an oxonium salt by a chromone[5] may, however, be taken as a distinguishing property.

In recent years ultraviolet absorption analysis has found wide application in the elucidation and corroboration of the structure of organic molecules.[6] Coumarins and chromones possessing characteristic chromophoric systems have received attention from time to time,[7,8,9] but sufficient systematic data required for identification purposes are still lacking. For this reason ultraviolet absorption studies of a number of coumarins and chromones have been undertaken with a view to ascertaining whether such studies can lead to any useful method for distinguishing between them.

In the present investigation emphasis will be placed on a correlation between ultraviolet absorption and molecular structure rather than on theoretical considerations. The compounds studied have been listed in Tables I and II. Absorption has been measured in the region 200–340 mμ, as beyond this range these compounds did not show significant absorption. It will be observed that the list contains the parent substances *viz.*, coumarin and chromone as well as their methyl derivatives substituted both in the aromatic and heterocyclic rings. The compounds were prepared by methods given in the literature, the methods being so selected as to avoid, as far as possible, any ambiguity about their molecular structure. These procedures are described under the experimental section. The products were very carefully purified by repeated crystallization so as to obtain sharp and constant melting points.

Measurements. Absorption measurements were taken on a Beckman Model D U Quartz Spectrophotometer using a 95% ethanolic solution at a concentration of around 6–7 mg. per liter.

Results. The absorption spectra are given in Figures 1–5. It will be observed that the absorption curves of coumarins form a family of closely related curves while those of chromones belong to a quite distinctive family. Their main absorption characteristics are summarized in Tables I and II.

Coumarins show one prominent minimum at 244 ± 4 mμ (log ϵ = 326–3.54), one principal maximum at 275 ± 4mμ (log ϵ = 3.98–4.10), a second minimum at 300 ± 5 mμ (log ϵ = 3.52–3.87) and a second maximum at 315 ± 8 mμ (log ϵ = 3.70–3.95). Only in one case *viz.*, that of 4,8-dimethylcoumarin, this second maximum and minimum are absent and a flat wave is observed in this region. In almost all cases the principal maximum and minimum are sharp and well defined but the second maximum and minimum except in a few cases are in general broad.

Chromones on the other hand invariably possess a strong maximum at 225 mμ (log ϵ = 4.33–4.42). Only in the case of chromone itself this maximum is below 220 mμ. These maxima are

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(1) Taken from the thesis submitted by B. K. Ganguly for the degree of Doctor of Philosophy (Science) of the University of Calcutta, January 1956.

(2) Chakravarti and co-workers, *J. Indian Chem. Soc.*, **8**, 129 (1931); **12**, 622 (1935); **13**, 649 (1936).

(3) Heilbron and co-workers, *J. Chem. Soc.*, 1263 (1933); 1311, 1581 (1934); 296 (1936).

(4) Heilbron, Barnes, and Morton, *J. Chem. Soc.*, **123**, 2559 (1923).

(5) Wittig, Bangert, and Richter, *Ann.*, **446**, 155 (1925).

(6) (a) Lewis and Calvin, *Chem. Revs.*, **25**, 273 (1939); (b) Ferguson, *Chem. Revs.*, **43**, 385 (1948); (c) Miller, *Gilman's Organic Chemistry*, Vol. III, John Wiley & Sons, New York, 1953, p. 122; (d) Braude, *Ann. Repts. on Prog. Chem.*, **42**, 105 (1945).

(7) Mangini and Passerini, *Bull. Sci. Facolta' Chim. ind. Bologna*, **9**, 54 (1951); Nakabayashi, Tokoroyama, Miyazaki and Isono, *J. Pharm. Soc. Japan*, **73**, 669 (1953).

(8) Jacobson, Brower, and Amstutz, *J. Org. Chem.*, **18**, 1117 (1953).

(9) Berson, *J. Am. Chem. Soc.*, **75**, 3521 (1953).

TABLE I

COUMARINS

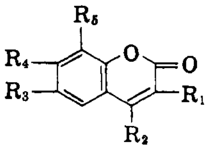
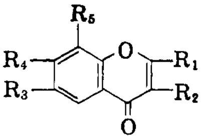
Serial No.		$\lambda_{min.1}$ (log ϵ)	$\lambda_{min.2}$ (log ϵ)	$\lambda_{max.1}$ (log ϵ)	$\lambda_{max.2}$ (log ϵ)
I	Coumarin $R_1 = R_2 = R_3 = R_4 = R_5 = H$	242 (3.2653)	298–299 (3.6857)	273.5 (4.0368)	307–309 (3.7449)
II	4-Methylcoumarin $R_1 = R_3 = R_4 = R_5 = H$ $R_2 = Me$	240.5 (3.2550)	294 (3.6395)	271 (3.9975)	307 (3.7559)
III	3-Methylcoumarin $R_2 = R_3 = R_4 = R_5 = H$ $R_1 = Me$	241.5 (3.3460)	297.5–298 (3.7736)	275 (4.0187)	308 (3.8029)
IV	3,4-Dimethylcoumarin $R_3 = R_4 = R_5 = H$ $R_1 = R_2 = Me$	243 (3.2655)	296 (3.7340)	273–273.5 (3.9841)	306–310 (3.8071)
V	4,8-Dimethylcoumarin $R_1 = R_3 = R_4 = H$ $R_2 = R_5 = Me$	248 (3.5411)	305–313 flat (3.7219)	276.5–278 (4.0953)	flat
VI	4,7-Dimethylcoumarin $R_1 = R_3 = R_5 = H$ $R_2 = R_4 = Me$	246 (3.2980)	297–297.5 (3.8656)	277–278.5 (4.0309)	314–315 (3.9543)
VII	4,6-Dimethylcoumarin $R_1 = R_4 = R_5 = H$ $R_2 = R_3 = Me$	242 (3.2838)	298.5 (3.5222)	273–273.5 (4.0086)	317–323 (3.6981)

TABLE II

CHROMONES

Serial No.		$\lambda_{max.1}$ (log ϵ)	Inflection or wave (log ϵ)	$\lambda_{min.1}$ (log ϵ)	$\lambda_{max.2}$ (log ϵ)
VIII	Chromone $R_1 = R_2 = R_3 = R_4 = R_5 = H$	—	245 inflection (3.9946)	270–271 (3.2246)	297–298 (3.8191)
IX	2-Methylchromone $R_2 = R_3 = R_4 = R_5 = H$ $R_1 = Me$	225 (4.3469)	245 inflection (3.9850)	273 (3.4919)	295 (3.9082)
X	3-Methylchromone $R_1 = R_3 = R_4 = R_5 = H$ $R_2 = Me$	225 (4.3326)	very slight inflection 245 (3.8872)	273.5–274 (3.2676)	304 (3.8705)
XI	2,3-Dimethylchromone $R_3 = R_4 = R_5 = H$ $R_1 = R_2 = Me$	225 (4.3885)	wave min 255 (3.7554) max 259 (3.7840) min 262 (3.7751) max 268 (3.8160)	277 (3.5145)	299–304 (3.9368)
XII	2,8-Dimethylchromone $R_2 = R_3 = R_4 = H$ $R_1 = R_5 = Me$	225 (4.4060)	wave min 238–240 (3.9607) max 248 (3.9946)	276–277 (3.5072)	299 (3.8663)
XIII	2,7-Dimethylchromone $R_2 = R_3 = R_5 = H$ $R_1 = R_4 = Me$	225 (4.3364)	wave min 245 (4.0718) max 247–248 (4.0778) min 256 (3.9099) max 266 (3.9533)	279.5 (3.7406)	294–295 (3.9074)
XIV	2,6-Dimethylchromone $R_2 = R_4 = H_5 = H$ $R_1 = R_3 = Me$	225 (4.4177)	245 inflection (4.0348)	276.5–278 (3.3907)	303 (3.8787)

followed by inflections at 245 mμ in the cases of chromone, 2-methylchromone, 3-methylchromone, and 2,6-dimethylchromone. In other cases these inflections are replaced by waves having very short crests in the region 245–268 mμ. Then come the principal minima at 275 ± 5 mμ (log ϵ = 3.22–3.74), followed by the second maxima at 300 ± 5 mμ (log ϵ = 3.82–3.94). The principal maxima and minima are quite sharp and well defined whereas the second maxima are more or less broad. Unlike the case of coumarins the second minima are absent here.

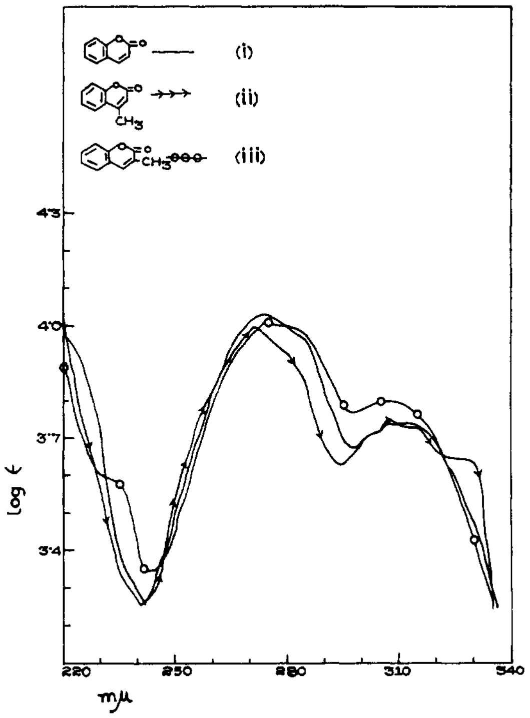


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF (I) Coumarin———; (II) 4-Methylcoumarin →→→; and (III) 3-Methylcoumarin —O—O—O—.

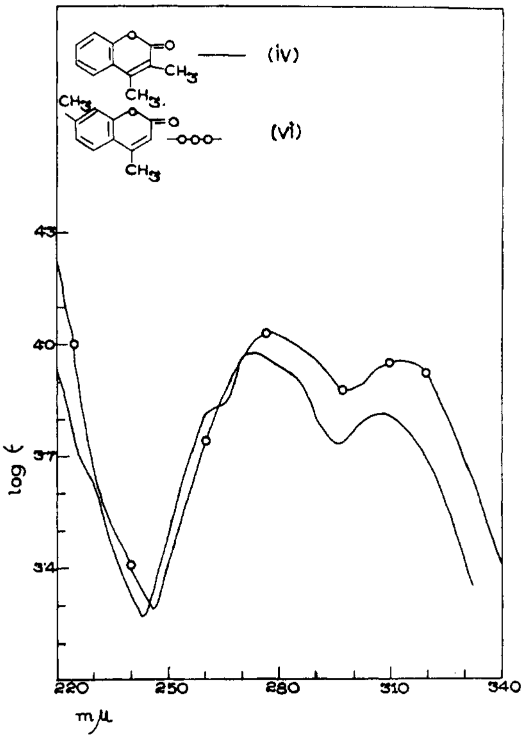


FIG. 2. ULTRAVIOLET ABSORPTION SPECTRA OF (IV) 3,4-Dimethylcoumarin ———; (VI) 4,7-Dimethylcoumarin —O—O—.

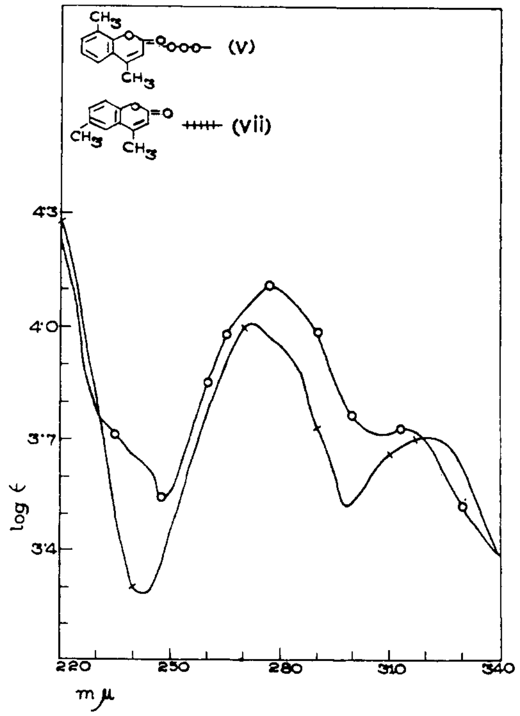


FIG. 3. ULTRAVIOLET ABSORPTION SPECTRA OF (V) 4,8-Dimethylcoumarin —O—O—O— and (VII) 4,6-Dimethylcoumarin —|—|—|—.

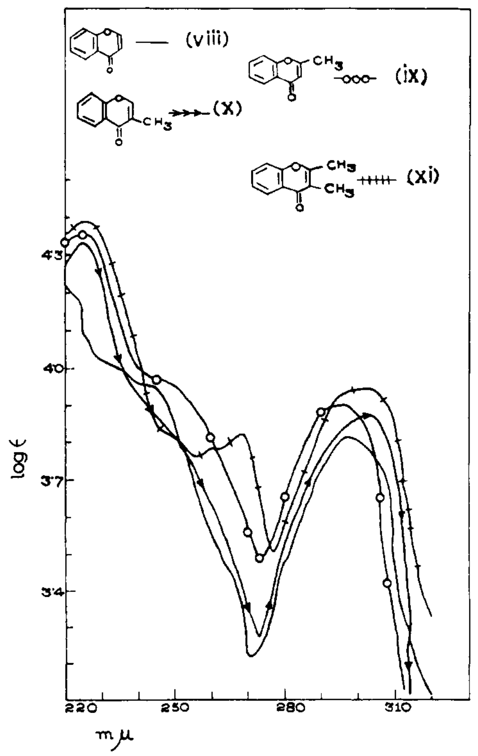


FIG. 4. ULTRAVIOLET ABSORPTION SPECTRA OF (VIII) Chromone———; (IX) 2-Methylchromone —O—O—O—; (X) 3-Methylchromone →→→; and (XI) 2,3-Dimethylchromone —|—|—|—.

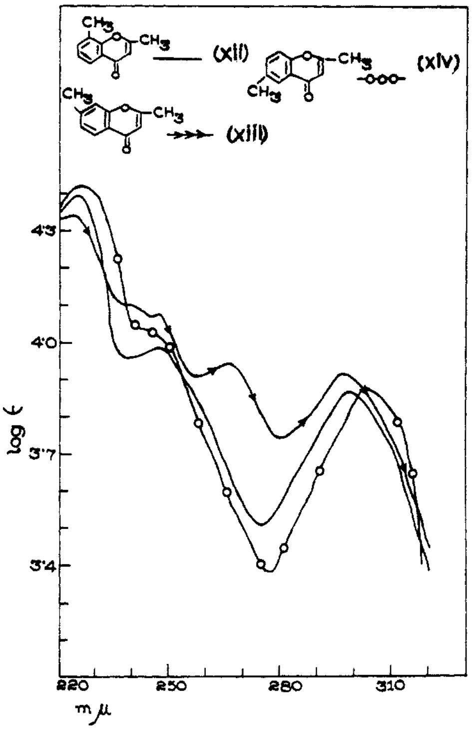


FIG. 5. ULTRAVIOLET ABSORPTION SPECTRA OF (XII) 2,8-Dimethylchromone ————; (XIII) 2,7-Dimethylchromone →→→→; and (XIV) 2,6-Dimethylchromone —O—O—O—.

It will be observed that the principal maxima of coumarins occur at higher wavelengths compared to those of chromones. This is evidently due to the presence of linear-conjugated systems in coumarins and cross-conjugated ones in chromones.[9a]

Study of auxochromic effect of the methyl group. A study of the data given in Table I will show that substitution of a hydrogen by methyl either in the heterocyclic or in the benzene ring of the coumarin molecule does not produce any significant change in the absorption properties, both the $\lambda_{max.}$ and the extinction coefficient remaining materially unchanged. It may be noted, however, that the principal minima in the case of 4,8-dimethyl- and 4,7-dimethyl-coumarin occurs at somewhat longer wave-lengths *viz.*, 248 mμ and 246 mμ respectively as against the usual range of 240.5–243 mμ for other coumarins studied. The principal maxima of the same coumarins are also at slightly higher wavelengths *viz.*, 276.5–278 mμ and 277–278.5 mμ respectively against the usual range of 271–275 mμ. But we do not consider these observations to be of much significance. In the case of chromones also, substitution of hydrogen by methyl fails to show any remarkable variation either in the position of the $\lambda_{max.}$ or $\lambda_{min.}$ or in the intensity of absorption.

Thus a study of the absorption spectra of coumarin, chromone, and their methyl derivatives will show that the most distinctive feature is the strong absorption (log ε greater than 3.8) in the 240–250 mμ range shown by chromones in contrast to the deep minima shown by coumarins in this range. Also the principal minima of coumarins and chromones are so characteristic and regular in their occurrence that they may be profitably utilized to characterize chromones and coumarins.

Study of absorption spectra of coumarins and chromones substituted with strong polar groups will form the subject of subsequent communications.

EXPERIMENTAL

All melting points are uncorrected.

The compounds were repeatedly crystallized from the solvents noted under respective headings until sharp and constant melting points were obtained.

Coumarin (I) was prepared by the method of Perkin[10] and was crystallized from petroleum ether (40–60°); m.p. 68°.

Anal. Calc'd for $C_9H_6O_2$; C, 73.9; H, 4.1. Found: C, 73.9; H, 4.0.

4-Methylcoumarin (II) was prepared by the method of Pechmann, *et al.*[11] and was crystallized from a benzene-petroleum ether (40–60°) mixture; m.p. 82°; lit.,[11] 82°.

Anal. Calc'd for $C_{10}H_8O_2$: C, 75.0; H, 5.0. Found: C, 74.7; H, 5.1.

3,4-Dimethylcoumarin (IV) was prepared by the method of Simonis, *et al.*[12] and was crystallized from ethanol; m.p. 115°; lit.,[12] 115°.

Anal. Calc'd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.7. Found: C, 75.5; H, 5.7.

4,8-Dimethylcoumarin (V) was prepared by the method of Chakravarti, *et al.*[13] and was crystallized from ethanol m.p. 115°; lit.,[13] 114°.

Anal. Calc'd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.7. Found: C, 76.0; H, 6.0.

4,7-Dimethylcoumarin (VI) was prepared by the method of Fries, *et al.*[13a] and was crystallized from ethanol; m.p. 132°; lit.,[23a] 132°.

Anal. Calc'd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.7. Found: C, 75.7; H, 5.9.

4,6-Dimethylcoumarin (VII) was prepared by the method of Chakravarti, *et al.*[13] and was crystallized from benzene; m.p. 151°; lit.,[13] 150°.

Anal. Calc'd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.7. Found: C, 76.1; H, 5.5.

3-Methylcoumarin (III). A mixture of salicylaldehyde (3.5 g.), ethyl α-bromopropionate (6.5 g.), zinc (4.8 g.), and dry benzene (30 c.c.) was heated to boiling and after the vigor of the reaction had subsided, refluxing was continued for one hour more. The flask then was allowed to cool and the benzene layer was poured into crushed ice containing hydrochloric acid. The benzene layer then was separated and the aqueous layer was extracted with benzene. The combined benzene solution was washed with dilute hydrochloric acid and water. After removal of benzene the residue was distilled at 152°/5 mm. when a colorless oil was obtained; yield 1.8 g. The above oil was hydrolyzed

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(9a) Fieser and Fieser, *Natural Products Related to Phenanthrene*, Reinhold Publishing Corporation, New York, 1949, p. 187; Elpern and Nachod, *J. Am. Chem. Soc.*, **72**, 3379 (1950).

(10) Perkin, *J. Chem. Soc.*, *21*, 53 (1863).

(11) Pechmann and Krafft, *Ber.*, **34**, 421 (1901).

(12) Simonis and Peters, *Ber.*, **41**, 830 (1908).

(13) Chakravarti and Dutta, *J. Indian Chem. Soc.*, **17**, 65 (1940).

(13a) Fries and Klostermann, *Ber.*, **39**, 871 (1906).

with aqueous sulfuric acid (20%) by refluxing for four hours. The flask then was cooled when a solid appeared. The solid was taken up in ether. The ether extract was washed with ice-cold sodium hydroxide solution (2%) and dried over sodium sulphate. Then the solvent was distilled off and the residue was repeatedly crystallized from ethanol until the melting point rose to 90°; lit.[14] m.p. 90°.

Anal. Calc'd for $C_{10}H_8O_2$: C, 75.0; H, 5.0. Found: C, 74.9; H, 4.9.

Chromone (VIII) was prepared by the method of Schönberg, *et al.*[15] and was crystallized from petroleum ether (40–60°); m.p. 59°; lit.,[15] 59°.

Anal. Calc'd for $C_9H_6O_2$: C, 73.9; H, 4.0. Found: C, 73.8; H, 4.0.

2-Methylchromone (IX) was prepared by the method of Badcock, *et al.*[16] and was crystallized from petroleum ether (40–60°); m.p. 73°; lit.,[16] 71°.

Anal. Calc'd for $C_{10}H_8O_2$: C, 75.0; H, 5.0. Found: 74.8; H, 5.0.

3-Methylchromone (X) was prepared by the method of Schönberg, *et al.*[17] and was crystallized from petroleum ether (40–60°); m.p. 70°; lit.,[17] 69°.

Anal. Calc'd for $C_{10}H_8O_2$: C, 75.0; H, 5.0. Found: C, 74.9; H, 4.9.

2,7-Dimethylchromone (XIII) was prepared from 2-acetyl-5-methylphenol and ethyl acetate by the method of Schönberg, *et al.*[15] The crude intermediate diketone which melted at 78° gave, after cyclization, the above chromone. The chromone was crystallized from benzene; m.p. 98–99°; lit.,[18] 98°.

Anal. Calc'd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.7. Found: 75.7; H, 5.5.

2,6-Dimethylchromone (XIV) was prepared from 2-acetyl-4-methylphenol and ethyl acetate by the method of Schönberg, *et al.*[15] The crude intermediate diketone melted at 98° and gave after cyclization, the above chromone which was crystallized from petroleum ether (60–80°); m.p. 103°; lit.,[19] 103°.

Anal. Calc'd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.7. Found: 75.9; H, 6.0.

2,3-Dimethylchromone (XI) was prepared by the method of Petschek, *et al.*[20] and was crystallized from benzene; m.p. 97°; lit.,[20] 97°.

Anal. Calc'd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.7. Found: C, 75.8; H, 5.6.

2,8-Dimethylchromone (XII) was prepared by the method of Simonis, *et al.*[21] and was crystallized from ethanol; m.p. 115°; lit.,[21] 115°.

Anal. Calc'd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.7. Found: C, 75.9; H, 5.7.

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[14] Baidakowsky, *J. Russ. Phys.-Chem. Soc.*, **37**, 902 (1905); Mentzer and Meunier, *Bull. soc. chim.*, **10**, 356 (1943).

[15] Schönberg and Sina, *J. Am. Chem. Soc.*, **72**, 3396 (1950).

[16] Badcock, Dean, Robertson and Whalley, *J. Chem. Soc.*, 903 (1950).

[17] Schönberg and Sina, *J. Chem. Soc.*, 3344 (1950).

[18] Zaki and Azzam, *J. Chem. Soc.*, 434 (1943).

[19] Baker, *J. Chem. Soc.*, 1381 (1933).

[20] Petschek and Simonis, *Ber.*, **46**, 2014 (1913).

[21] Simonis and Lehmann, *Ber.*, **47**, 697 (1914).