220. *Synthetical Experiments in the Chromone Group. Part IX. A Synthesis of 5 : 7 : 4′-Trihydroxy-3′ : 5′-dimethoxyflavone, believed to be Identical with Tricin.*

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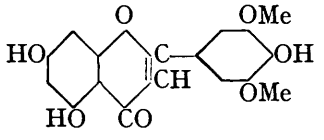
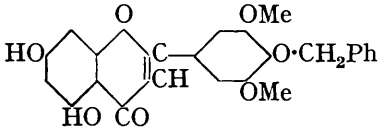
The validity of the suggestion (Venkataraman, *Current Science*, 1933, **1**, 238) that tricin, the colouring matter of " Khapli " wheat (Anderson and Perkin, J., 1931, 2624; Anderson, *Canadian J. Res.*, 1932, **7**, 285), is the 3′ : 5′-dimethyl ether (I) of 5 : 7 : 3′ : 4′ : 5′-pentahydroxyflavone (tricetin) has now been tested by synthesis, the method used by Heap and Robinson (J., 1929, 67) in the case of syringetin being employed. The interaction of phloracetophenone with *O*-benzylsyringic anhydride and sodium *O*-benzylsyringate, followed by vigorous alkaline hydrolysis, led to 5 : 7-*dihydroxy*-3′ : 5′-*dimethoxy*-4′-*benzyloxyflavone* (II); debenzylation with hydrochloric acid in acetic acid yielded (I), whose properties (m. p., colour reactions, and m. p. of the *O*-triacetyl derivative) were in agreement with those of natural tricin.

(I.) 



(II.)

The penta-acetyl derivative of synthetic 5 : 7 : 3′ : 4′ : 5′-pentahydroxyflavone was found by Bargellini and Monti (*Gazzetta*, 1915, **45**, 64) to melt at 216—218° and by Anderson at 241—242°. The acetylation of the pentahydroxyflavone of Badhwar, Kang, and Venkataraman (J., 1932, 1107) has confirmed Anderson's observation. The flavone itself, after repeated crystallisation, darkened and decomposed gradually above 310° as stated by Badhwar and others (compare Anderson, *loc. cit.*).

Experimental.

5 : 7 : 3′ : 4′ : 5′-*Penta-acetoxyflavone*.—Acetylation of the pentahydroxyflavone of Badhwar *et al.* (*loc. cit.*) and two crystallisations from alcohol gave colourless needles, m. p. 241—242°; a portion appeared to remain semi-solid and complete clarification took place only at 246—248° [Found (microanalysis by Schoeller): C, 58·2; H, 4·1. Calc. for $C_{25}H_{20}O_{12}$: C, 58·6; H, 3·9%].

5 : 7-*Dihydroxy*-3′ : 5′-*dimethoxy*-4′-*benzyloxyflavone* (II).—A mixture of phloracetophenone (5 g.), *O*-benzylsyringic anhydride (35 g.), and sodium *O*-benzylsyringate (6 g.) was heated at 180—185° for 7 hours. The product was refluxed with 10% alcoholic potassium hydroxide

(140 c.c.) for 45 minutes and poured into water (1 l.), and the deep orange turbid solution saturated with carbon dioxide. A dark brown oil separated together with an orange solid; both were collected and boiled with 2·5% aqueous potassium hydroxide (100 c.c.) for 15 minutes. The liquid was filtered and again saturated with carbon dioxide. The deep orange powder which slowly separated was crystallised from acetic acid and then from aqueous acetone, forming pale orange, stout, prismatic needles (0·4 g.), m. p. 234° [Found (micro.): C, 68·6; H, 4·9. $C_{24}H_{20}O_7$ requires C, 68·6; H, 4·8%]. The substance dissolves in sulphuric acid with a pale yellow colour and no fluorescence and in aqueous sodium hydroxide with a pale yellow colour; an alcoholic solution is turned greenish-brown by ferric chloride.

5 : 7 : 4′-*Trihydroxy*-3′ : 5′-*dimethoxyflavone* (I).—To (II) (0·2 g.) in acetic acid (15 c.c.) heated on the water-bath, concentrated hydrochloric acid (1 c.c.) was added drop by drop; the red mixture turned to a clear yellow solution. More acid (1 c.c.) was added, and the heating continued for ½ hour. Dilution with water gave a pale yellow precipitate, which was crystallised twice from 70% alcohol. The pale old-gold yellow needles sintered at 278° and melted at 286—287° (tricin has m. p. 288°) [Found (micro.): C, 61·5; H, 4·3. Calc. for $C_{17}H_{14}O_7$: C, 61·8; H, 4·2%]. The pale yellow solution of the substance in sulphuric acid exhibited no fluorescence; the other reactions were identical with those described for tricin (Anderson and Perkin, *loc. cit.*). The acetyl derivative crystallised from alcohol in colourless silky needles, m. p. 249—251° (triacetyl tricin, 251—254°) [Found (micro.): C, 60·5; H, 4·6. Calc. for $C_{23}H_{20}O_{10}$: C, 60·5; H, 4·5%]. Deacetylation with hot 50% hydrochloric acid and crystallisation from alcohol gave (I) in pale yellow, ¼ cm.-long needles, m. p. 286—287°.

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