ylene chloride and dried with magnesium sulfate. Upon filtration and removal of the solvent by concentration under reduced pressure, the resulting sirup was dissolved in a minimum quantity of absolute methanol and seeded. After 6 days the crystalline product (211 mg., 50%) was collected. It showed a rotation of +58° (dioxane) and melted at 132–135° yielding a cloudy melt which became clear at 138°. There was no depression of the melting point when admixed with the 2-deoxy-3,5-di-*O*-*p*-nitrobenzoyl-D-ribose prepared as described above.

p-Nitrobenzoylation of 2-deoxy-3,5-di-O-p-nitrobenzoyl-D-ribose (VI). One gram of 2-deoxy-3,5-di-*O*-*p*-nitrobenzoyl-D-ribose (2.3 mmoles) was added to an ice-cold solution of 0.86 g. of *p*-nitrobenzoyl chloride (4.6 mmoles) in 15 ml. of pyridine. The solution was left at 0° for 10 min. and then at room temperature overnight. It was then cooled, treated with a little water, and diluted with 100 ml. of methylene chloride. The solution was washed successively with water, 3*N* sulfuric acid, saturated aqueous sodium bicarbonate, and water. It was then dried with sodium sulfate and concentrated to a sirup (1.34 g., 100%) which showed $[\alpha]_D^{20}$ +58° in chloroform (*c* 2). If this consisted solely of the anomeric 2-deoxy-D-ribofuranose tri-*p*-nitrobenzoates,[2] its rotation indicates that it contained 76% of the α-anomer. From chloroform–pentane solution the material deposited 740 mg. of crystalline product. Recrystallized from chloroform–pentane the ester (590 mg., 44%) was dried *in vacuo* overnight at 100°: m.p. 160–161°, $[\alpha]_D^{20}$ +71.6° (chloroform, *c* 0.5). Mixed with an authentic sample of 2-deoxy-α-D-ribofuranose tri-*p*-nitrobenzoate it melted at 160–162°. Ness and Fletcher[2] reported $[\alpha]_D^{20}$ +70.7° (chloroform) for the substance.

On standing, the mother liquors from the first crystallization above deposited 223 mg. of crystalline material. This was recrystallized from chloroform–pentane and dried at 100° *in vacuo* overnight: 154 mg. (11%), m.p. 162–164°, resolidifying and then melting at 168–170°, $[\alpha]_D^{20}$ +15.3° (chloroform, *c* 0.5). 2-Deoxy-β-D-ribofuranose tri-*p*-nitrobenzoate[2] melts at 172–173° and shows $[\alpha]_D^{20}$ +17.1° in chloroform.

Pyrolysis of 2-deoxy-3,5-di-O-p-nitrobenzoyl-D-ribosyl chloride (IV). 2-Deoxy-3,5-di-*O*-*p*-nitrobenzoyl-D-ribosyl chloride (164.9 mg.) was placed in a tared flask which was then evacuated to *ca.* 36 mm. and immersed in an oil bath (110–112°) for 2.5 min. On reweighing, the material was found to have lost 13.0 mg. or 7.9%. Loss of one mole equivalent of hydrogen chloride is calculated as 8.1%. The residue was dissolved in methylene chloride–ether solution and the solution extracted with sodium bicarbonate solution. Acidification of the aqueous extract yielded 57.1 mg. (93%) of *p*-nitrobenzoic acid, melting at 238–240°. The organic layer was dried with sodium sulfate, filtered through a little decolorizing carbon and concentrated *in vacuo* to a sirup (80.9 mg.). Several milliliters of hot absolute alcohol was added, the mixture centrifuged and the alcoholic layer decanted; on standing it deposited 11.2 mg. (12%) of crystalline material melting at 74–76°. Mixture with an authentic sample of furfuryl *p*-nitrobenzoate[3] (m.p. 76–77°) did not depress this melting point. In chloroform solution the infrared spectra of the product and of the authentic material were identical.

Acknowledgment. We are indebted to the Analytical Services Unit of this Laboratory under the direction of Mr. H. G. McCann for analyses.

BETHESDA 14, Md.

[CONTRIBUTION FROM THE FRUIT AND VEGETABLE CHEMISTRY LABORATORY, WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION, AGRICULTURAL RESEARCH SERVICE, UNITED STATES DEPARTMENT OF AGRICULTURE]

Flavonoids of Citrus. V. Structure of Limocitrin[1]

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Limocitrin, a new flavonol isolated from lemons, is shown to be 3′,8-dimethoxy-3,5,7,4′-tetrahydroxyflavone. A synthesis of 5-*O*-methyllimocitrin is described and spectral data are presented for limocitrin and a number of related compounds.

Extracts of lemon peel (*Citrus limon*) contain a number of phenolic glycosides which can be hydrolyzed enzymatically by crude preparations of hemicellulase. The product of this hydrolysis is a mixture of polyphenols from which various flavonoid aglycones, coumarins and substituted cinnamic acids have been separated and identified.[2] Many of these compounds were not previously recognized as constituents of the lemon, although they had been obtained earlier from other plant sources. Several of the compounds are new, however, and one of these will be described here.

The crude hydrolytic products can be conveniently divided into an ether soluble and ether insoluble fraction. On standing for several days the ether soluble fraction deposits a small amount of a pure, crystalline yellow solid, m.p. 274–275°. A slightly better yield of the substance is obtained by chromatographing this fraction on a column of silicic acid which is eluted with chloroform-acetone. The compound can be recognized as a flavonol by the magenta color obtained on reduction with magnesium in hydrochloric acid and by its ultraviolet spectra in ethanol, and in ethanol saturated with aluminum chloride (Table I). We propose to name the new flavonol *limocitrin*.

Limocitrin contains two methoxyl and four hydroxyl groups as shown by analyses of the compound itself and its tetraacetyl and tetraethyl derivatives. The location of one of the methoxyl groups at the 3′-position and one of the hydroxyl groups at the 4′-position followed from the identification of vanillic acid among the alkaline cleavage products.

Methylation of limocitrin with excess methyl sulfate yields a permethyl ether which has the same ultraviolet spectrum as that recorded[3] for 3,5,7,8,3′,4′ - hexamethoxyflavone (gossypetin hex-

(1) A preliminary account of this work has appeared: R. M. Horowitz, *J. Am. Chem. Soc.*, 79, 6561 (1957).

(2) R. M. Horowitz and B. Gentili, *J. Org. Chem.*, 25, 2183 (1960).

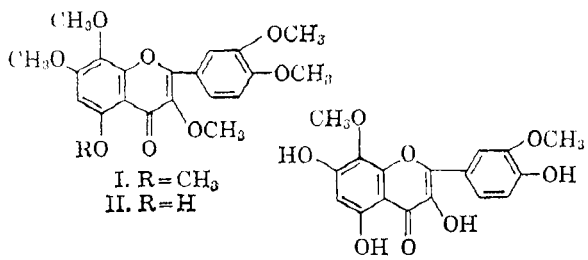
TABLE I

ABSORPTION SPECTRA OF LIMOCITRIN AND DERIVATIVES

Compound	λ_{max} in mμ: Absolute C_2H_5OH	Short wave-length band in NaOAc—C_2H_5OH[b]	Long wave-length band in NaOH—C_2H_5OH[c]	Long wave-length band in NaOAc—H_3BO_3—C_2H_5OH[d]	Long wave-length band in $AlCl_3$—C_2H_5OH[e]
Limocitrin (III)	259, 273[a], 340,[a] 378	282	Dec.	379	442
5,8,3′-Trimethoxy-3,7,4′-trihydroxyflavone (VI)	255, 272,[a] 370	281	Dec.		445
4′-Benzyloxy-5,8,3′-trimethoxy-3,7-dihydroxyflavone (V)	255, 272,[a] 368	282	415		432

[a] Inflection. [b] Absolute alcohol saturated with fused sodium acetate. [c] One drop of 1% sodium hydroxide added to 2.5 ml. cuvette. Sodium ethylate is specified in ref. 4, but the same results are obtained using sodium hydroxide. [d] Ref. 5. [e] Ethanol solution saturated with aluminum chloride.

amethyl ether) (I). The identity of the permethyl ether with I was confirmed by comparison with a synthetic specimen. It remained to determine which position (3, 5, 7, or 8) carries the second methoxyl group. As limocitrin, unlike flavones containing free *p*-hydroxyl groups, fails to undergo aerial oxidation to deeply colored substances in alkaline solution and fails to color when treated with *p*-benzoquinone in alcohol (the "gossypetone" reaction), it was apparent that the second methoxyl must be situated at either the 5- or 8-position. The possibility of a 5-methoxyl group was eliminated by the fact that limocitrin, on treatment with three moles of methyl sulfate, yields 5-hydroxy-3,7,8,-3′,4′-pentamethoxyflavone (II). It follows that limocitrin must be 3′,8-dimethoxy-3,5,7,4′-tetrahydroxyflavone (III).

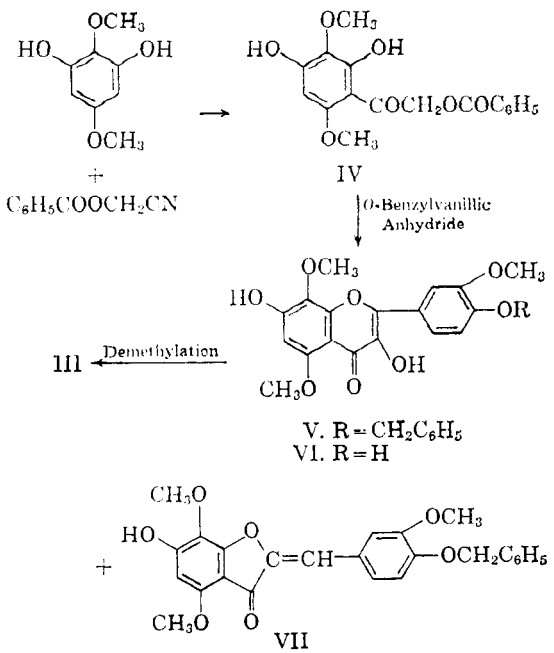


I. R = CH_3
II. R = H

III. Limocitrin

To confirm this structure we applied a previously reported[4] spectral procedure for determining the presence of certain hydroxyl groups in flavonols. In this procedure one notes the spectral changes which occur when (1) fused sodium acetate, (2) sodium ethylate, and (3) sodium acetate–boric acid are added to a solution of a flavonol in absolute ethanol. It has been found that a bathochromic shift of the short wave-length band with fused sodium acetate indicates the presence of a free 7-hydroxyl group; that the disappearance of the long wave-length band (rather than a bathochromic shift) with sodium ethylate indicates the simultaneous presence of free 3- and 4′-hydroxyl groups; and that a bathochromic shift with sodium acetate–boric acid[5] indicates the presence of *o*-hydroxyl groups. When these tests were applied to limocitrin the results showed clearly that the compound has free hydroxyl groups at positions 7, 3, and 4′ and has no *o*-hydroxyl groups. The spectral curves illustrating this are shown in Fig. 1. Structure III is the only dimethyl ether of gossypetin which can accomodate these spectral data.

It was planned to synthesize limocitrin by the following reactions:



The Hoesch reaction of 2,5-dimethoxyresorcinol with benzoyloxyacetonitrile proceeded as expected to give the ω-benzoyloxyacetophenone derivative IV. This on treatment with *O*-benzylvanillic an-

(3) L. H. Briggs and R. H. Locker, *J. Chem. Soc.*, 3136 (1951).

(4) L. Jurd and R. M. Horowitz, *J. Org. Chem.*, 22, 1618 (1957).

(5) L. Jurd, *Arch. Biochem. Biophys.*, 63, 376 (1956).

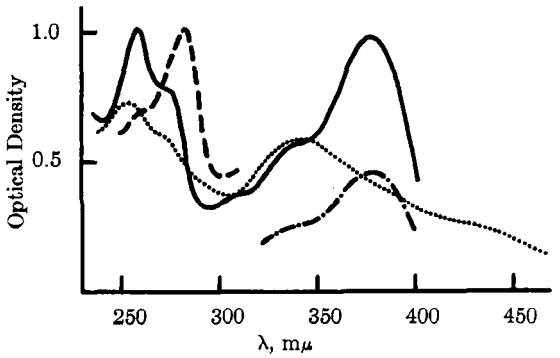


Fig. 1. Absorption spectra of limocitrin: ——— absolute ethanol; ——— fused sodium acetate added; ..... sodium hydroxide added and allowed to stand five minutes; -·-·- sodium acetate–boric acid added (solution diluted)

hydride in the presence of triethylamine,[6] gave a small yield of 4′-benzyloxy-5,8,3′-trimethoxy-3,7-dihydroxyflavone (V), which was debenzylated by catalytic hydrogenation to 5,8,3′-trimethoxy-3,7,4′-trihydroxyflavone (VI). However, attempts to convert VI to limocitrin by selective demethylation of the 5-methoxyl group were uniformly unsuccessful. A number of demethylating reagents were tried, including aniline hydrochloride, aluminum chloride in various solvents, and hydriodic and hydrobromic acids. In each case, however, the compound was recovered unchanged, or else appeared to have undergone total demethylation.

As compound VI could not be converted to limocitrin, the inverse procedure of converting limocitrin to VI was carried out. Partial acetylation of limocitrin by the procedure of Simokoriyama[7] gave 3,7,4′-tri-*O*-acetyllimocitrin, which, on methylation at the 5-position followed by deacetylation, gave 5-*O*-methyllimocitrin. This was identical with VI and the proof of structure was completed.

In several runs involving the condensation of compound IV with *O*-benzylvanillic anhydride, a small amount of a deep orange, crystalline by-product was isolated. It was apparent from its ultraviolet spectrum that the compound is an aurone and, therefore, its structure may be written as 4′-benzyloxy-4,7,3′-trimethoxy-6-hydroxy-benzalcoumaranone (VII).[8] This structure is supported by analytical data obtained on its acetyl derivative. It is not clear how the compound is formed, however, as a reduction must occur at some stage. Triethylamine, the catalyst used for this condensation, might conceivably act as the reducing agent, but the nature of the reaction is obscure.

EXPERIMENTAL

Isolation of limocritin. "Calcium Flavonate Glycoside, Lemon"[9] (100 g.) suspended in 0.1*M* acetate buffer (1800 ml.; *p*H 4.5) was warmed on the steam bath for 30 min. to effect partial solution. The mixture was filtered and the *p*H of the filtrate was readjusted to 4.6 with acetic acid. Hemicellulase (5 g.; Nutritional Biochemicals Corp.) suspended in acetate buffer (25 ml.) was added with shaking and the mixture kept for 24 hr. at 27°. More hemicellulase (2 g.) was then added and the mixture kept an additional 24 hr. when the hydrolysis appeared complete as indicated by Bryant's test.[10] The mixture was extracted with ethyl acetate (4 × 250 ml.) which, on evaporation, yielded a yellow-brown semi-crystalline solid. This was boiled under reflux with two 100-ml. portions of ether for 90 and 30 min., respectively. (The solid not dissolved by ether was crude eriodictyol (3.4 g.).)[11]

The combined ether extract was concentrated to a volume of 20 ml. and allowed to stand several days until crystallization took place. The crude material was collected (120 mg.; m.p. 255–265°) and recrystallized several times from acetone-methanol. Limocitrin was obtained as bright yellow rosettes (46 mg.), m.p. 274–275° (subl.).

In other runs limocitrin was obtained in somewhat better yield by chromatographing the ether extract on silicic acid. This procedure has been described in detail.[2]

Anal. Calcd. for $C_{17}H_{14}O_8$: C, 59.0; H, 4.08; 2 CH_3O, 17.9. Found: C, 58.8; H, 4.27; CH_3O, 18.7.

Limocitrin is sparingly soluble in methanol, ethanol acetone, and water but dissolves in dilute alkali with formation of a yellow color. It gives a green ferric test and turns deep red on reduction with magnesium in hydrochloric acid. It reduces Tollens' reagent to a slight extent only, as do kaempferol and other flavonols containing free hydroxyl groups in both the 3- and 4′-positions. (Flavonols containing *o*- or *p*-hydroxyl groups give much more intense reduction.) Solutions of the substance in ethanol containing *p*-benzoquinone remain yellow indefinitely, while solutions of gossypetin or gossypetin 7-glucoside turn deep red within minutes. Limocitrin has an R_f value of 0.45 in acetic acid–water (1:1) (brown-yellow in ultraviolet light changing to dull yellow with aluminum chloride).

Alkaline hydrolysis of limocitrin. A solution of limocitrin (23 mg.) in 60% potassium hydroxide (2 ml.), boiled under reflux for 45 min., yielded crystals of vanillic acid, m.p. and mixed m.p. (after sublimation) 209°; $\lambda_{max}^{C_2H_5OH}$ 260,290 mμ; $\lambda_{max}^{C_2H_5OH-NaOH}$ ~ 280, 295 mμ; R_f 0.82 in benzene–acetic acid–water (2:2:1).

3,5,7,4′-Tetra-O-acetyllimocitrin. This was prepared in the usual way in hot acetic anhydride–sodium acetate, m.p. 155–156° (ethyl acetate–ether); $\lambda_{max}^{C_2H_5OH}$ 243, ~ 260, 318 mμ.

Anal. Calcd. for $C_{25}H_{22}O_{12}$: C, 58.4; H, 4.31; 2 CH_3O, 12.1. Found: C, 58.3; H, 4.37; CH_3O, 12.4.

3,5,7,4′-Tetra-O-ethyllimocitrin. A mixture of limocitrin (23.4 mg.), ethyl sulfate (0.1 ml.), potassium carbonate (0.5 g.), and acetone (50 ml.) was boiled under reflux for 6 hr. As the product still gave a positive ferric test, it was taken up in hot ethanol and treated with alternate portions of ethyl sulfate and aqueous sodium hydroxide until the yellow color disappeared. Dilution with water yielded fine, colorless needles which were recrystallized from dilute methanol, m.p. 116° (resolidifying) and 130°; $\lambda_{max}^{C_2H_5OH}$ 253, 272, 351 mμ.

Anal. Calcd. for $C_{25}H_{30}O_8$: C, 65.4; H, 6.59; Alkoxyl (cal-

(6) This is the Kostanecki-Robinson reaction as modified by R. Kuhn and I. Löw: *Ber.*, **77B**, 196 (1944).

(7) M. Simokoriyama, *Bull. Chem. Soc. Japan*, **16**, 284 (1941).

(8) Aurone spectra are discussed by T. A. Geissman and J. B. Harborne, *J. Am. Chem. Soc.*, **78**, 832 (1956).

(9) This is a mixture of the flavonoid glycosides of lemon peel prepared as calcium salts; manufactured by Lemon Products Division, Sunkist Growers, Corona, Calif.

(10) E. F. Bryant, *J. Am. Pharm. Assoc., Sci. Ed.*, **39**, 480 (1950).

(11) R. M. Horowitz and B. Gentili, *J. Am. Chem. Soc.*, **82**, 2803 (1960).

culated as CH_3O), 40.6. Found: C, 65.6; H, 6.68; CH_3O, 40.9.

3,5,7,8,3',4'-Hexamethoxyflavone (I). A solution of limocitrin in hot ethanol was treated with alternate portions of methyl sulfate and 6*N* sodium hydroxide until further addition of alkali gave no intensification of color. Fine, pale yellow needles separated after several hours. These, on recrystallization from dilute ethanol, had m.p. 148–150° (resolidifying) and 168–169°, not depressed on mixing with synthetic 3,5,7,8,3',4'-hexamethoxyflavone,[12] the reported m.p. of which is 170–172°.[12,13] The ultraviolet spectrum ($\lambda_{max}^{C_2H_5OH}$ 252, 272, 351 mμ) agreed closely with that of the latter compound.[8]

5-Hydroxy-3,7,8,3',4'-pentamethoxyflavone (II). A mixture of limocitrin (15.8 mg.), methyl sulfate (17.9 mg. 3 moles), potassium carbonate (0.5 g.) and acetone (50 ml.) was boiled under reflux for 3 hr. The product obtained by filtration and evaporation crystallized as yellow prisms from ethanol, m.p. 156–157°, not depressed on mixing with synthetic 5-hydroxy-3,7,8,3',4'-pentamethoxy flavone (see below); $\lambda_{max}^{C_2H_5OH}$ 257, 275, ~ 340, 360 mμ.

The *5-O-acetyl* derivative crystallized from ethyl acetate–ether as colorless needles, m.p. 162°, not depressed on mixing with an authentic specimen (see below); $\lambda_{max}^{C_2H_5OH}$ 250, 346 mμ.

Methylation of 5,8-dihydroxy-3,7,3',4'-tetramethoxyflavone[12] with 1 mole of methyl sulfate in the presence of potassium carbonate and acetone gave 5-hydroxy-3,7,8,3',4'-pentamethoxyflavone, yellow prisms from ethanol, m.p. 157–158°; reported m.p. 166–167°.[14]

Anal. Calcd. for $C_{20}H_{20}O_8$: C, 61.9; H, 5.19; 5 CH_3O, 39.9. Found: C, 62.0; H, 5.26; CH_3O, 39.7.

5-Acetoxy-3,7,8,3',4'-pentamethoxyflavone crystallized from ethyl acetate–ether as colorless needles, m.p. 163°.

Anal. Calcd. for $C_{22}H_{22}O_9$: C, 61.4; H, 5.15. Found: C, 61.3; H, 5.24.

2,4-Dihydroxy-3,6-dimethoxy-ω-benzoyloxyacetophenone (IV). A stirred solution of 2,5-dimethoxyresorcinol[13,15] (6.0 g.) and benzoyloxyacetonitrile[16] (5.5 g.) in anhydrous ether (100 ml.) was kept in an ice bath for 4.5 hr. during which a slow stream of dry hydrogen chloride was passed through. The precipitated ketimine was collected, washed with ether, and dissolved in 50% aqueous ethanol (200 ml.). This solution was boiled under reflux for 5 hr., then was set aside for crystallization to be completed. The product was recrystallized from benzene as colorless plates, m.p. 177° (yield 51%); $\lambda_{max}^{C_2H_5OH}$ 293 mμ.

Anal. Calcd. for $C_{17}H_{16}O_7$: C, 61.4; N, 4.85; CH_3O, 18.7 Found: C, 61.6; H, 4.95; CH_3O, 18.9.

4'-Benzyloxy-5,8,3'-trimethoxy-3,7-dihydroxyflavone (V). A mixture of 2,4-dihydroxy-3,6-dimethoxy-ω-benzoyloxyacetophenone (2.0 g.), *O*-benzylvanillic anhydride (12.0 g.), and triethylamine (4.2 ml.) was heated at 160–170° for 6 hr. The product was boiled for 30 min. with ethanol (250 ml.) and 6*N* sodium hydroxide (50 ml.). The mixture was then evaporated under vacuum to remove alcohol while keeping the volume at 200 ml. by addition of water. Excess carbon dioxide was passed in and the mixture was finally extracted with ethyl acetate (20 × 50 ml.). On partial evaporation the ethyl acetate deposited yellow rectangular plates (0.3 g.), m.p. 238–241°, raised to 247–249° on recrystallization from glacial acetic acid. The compound exhibited color reactions and absorption spectra typical of a flavonol (Table I). (The ethyl acetate liquors yielded the aurone VII, as described below.)

Anal. Calcd. for $C_{25}H_{22}O_8$: C, 66.7; H, 4.92; CH_3O, 20.7. Found: C, 66.6; H, 4.99; CH_3O, 20.6.

5,8,3'-Trimethoxy-3,7,4'-trihydroxyflavone (VI). The preceding compound (264 mg.) dissolved in acetic acid (250 ml.) containing 30% palladium-charcoal (150 mg.) was shaken with hydrogen until absorption was complete. The residue obtained after filtration and evaporation crystallized from ethanol as yellow plates (130 mg.), m.p. 236–237°. Solutions or paper chromatograms of the compound fluoresced bright yellow when examined under ultraviolet light.

Anal. Calcd. for $C_{18}H_{16}O_8$: C, 60.0; H, 4.48; CH_3O, 25.8. Found: C, 59.7; H, 4.53; CH_3O 25.7.

3,7,4'-Tri-O-acetyllimocitrin. A mixture of limocitrin (44 mg.), acetic anhydride (0.5 ml.), and pyridine (1 drop) was shaken at room temperature for 3–4 min. until it set to a mass of yellow needles. The product recrystallized from acetone-methanol had m.p. 188–189° and gave an emerald green ferric test; $\lambda_{max}^{C_2H_5OH}$ 248 (low), 273, 315 (low), ~350 mμ

Anal. Calcd. for $C_{23}H_{20}O_{11}$: C, 58.5; H, 4.27; $COCH_3$, 27.3; CH_3O, 13.1. Found: C, 58.7; H, 4.24; $COCH_3$, 28.0; CH_3O, 13.2.

5-O-Methyllimocitrin. A mixture of 3,7,4'-tri-*O*-acetyllimocitrin (40.5 mg.), methyl iodide (1 ml.), potassium carbonate (0.5 g.), and acetone (15 ml.) was boiled under reflux until the yellow color disappeared (75 min.). The product obtained on filtration and evaporation was deacetylated in hot methanol-hydrochloric acid (2:1) and was then crystallized from ethyl acetate–acetone. On recrystallization from ethanol it was obtained as stubby needles, m.p. 234–235°, not depressed on mixing with 5,8,3'-trimethoxy-3,7,4'-trihydroxyflavone. The infrared and ultraviolet spectra (Table I) were identical with those of the latter compound.

4'-Benzyloxy-4,7,3'-trimethoxy-6-hydroxybenzalcoumaranone (VII). The ethyl acetate liquors from the preparation of compound V were taken to dryness and the solid residue was recrystallized first from ethanol, then from acetic acid. The main product was benzylvanillic acid. On standing, the acetic acid liquors yielded a small quantity (60 mg.) of impure, yellow-orange crystals, m.p 200–217°; $\lambda_{max}^{C_2H_5OH}$ 252 (low), ~270, ~320, ~390, 404 mμ. The compound gave a deep red color in concentrated sulfuric or hydrochloric acid.

The impure solid was acetylated in the usual way with acetic anhydride–sodium acetate and the product recrystallized from ethyl acetate–methanol and ethyl acetate–ether. It was finally obtained as bright yellow needles, m.p. 225–226°; $\lambda_{max}^{C_2H_5OH}$ 271 (low), 317 (low), 416 mμ.

Anal. Calcd. for $C_{27}H_{24}O_8$: C, 68.1; H, 5.08; $COCH_3$, 9.03; 9.03; CH_3O, 19.5. Found: C, 68.1; H, 5.16; $COCH_3$, 9.35; CH_3O, 19.7.

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(16) J. Aloy and C. Rabaut, *Bull. Soc. Chim.*, **13**, 457 (1913).