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Synthetic Studies of the Flavone Derivatives. XVII.*[1] Synthesis of 5,7-Dihydroxy-6-methoxyflavone Derivatives[2]*

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2,4-Dibenzyloxy-6-hydroxy-3-methoxyacetophenone was esterified with 3,4-disubstituted benzoyl chlorides, and the resulting esters were converted into 7-benzyloxy-5-hydroxy-6-methoxyflavone derivatives *via* the corresponding diketones. The catalytic hydrogenolysis of the benzyloxyflavones gave the desired 5,7-dihydroxy-6-methoxyflavones. Ethyl ethers of these flavones were also prepared from 2,4-diethoxy-3-methoxy-6-hydroxyacetophenone by an unambiguous method. 6,3′-Dimethoxy-5,7,4′-trihydroxyflavone, desmethoxycentaureidin (6,4′-dimethoxy-5,7,3′-trihydroxyflavone), and 6-methoxyluteolin (6-methoxy-5,7,3′,4′-tetrahydroxyflavone) were thus prepared.

Recently 6,3′-dimethoxy-5,7,4′-trihydroxyflavone (Ia) has been isolated from *Digitalis lanata* L.,[1] *Helichrysum visocum* var. *bracteatum* DC.,[2] and *Helenium alternifolium* (Spreng) Cabrera,[3] desmethoxycentaureidin (6.4′-dimethoxy-5,7,3′-trihydroxyflavone) (Ib) has been isolated from *Centaurea nigrescens* Willd,[4] and 6-methoxyluteolin[5] (nepetin[6]) (6-methoxy-5,7,3′,4′-tetrahydroxyflavone*[3]) (Ic) has been isolated from *Rosmarinus officinalis* L.[5] and *Nepeta hindostana*.[6]

This paper will report on the syntheses of these 5,7-dihydroxy-6-methoxyflavone derivatives (Ia-c) and will attempt to confirm the structure.

2,4-Dibenzyloxy-6-hydroxy-3-methoxyacetophenone (II)[7] was prepared from 3-methoxy-2,4,6-trihydroxyacetophenone[8] by partial benzylation, it was then esterified with 3,4-disubstituted benzoyl chlorides, such as 4-benzyloxy-3-disubstituted benzyloxy-4-methoxy-(b), and 3,4-dibenzyloxy-(c)-chloride, in the presence of anhydrous pyridine. The resulting esters were converted into ω-(3,4-disubstituted benzoyl)-2,4-dibenzyloxy-6-hydroxy-3-methoxyacetophenones (IIIa-c) by Baker-Venkataraman transformation.[9] The cyclodehydration of the acetophenones (IIIa-c) with anhydrous sodium acetate in acetic acid afforded flavones (IVa-c). The UV spectra of the flavones (IVa-c) showed the bathochromic shift of Bands I and II in the presence of aluminum chloride (Table 3). The NMR spectra*[4] of IIIa-c indicated the presence of a chelated phenolic group. The spectra exhibit, further, reasonable signals of the aromatic-, benzyloxy-, and methoxy-protons (Table 1).

These facts indicate that IVa-c were obtained from IIIa-c by the cyclodehydration with anhydrous

*1 Part XVI of this series: K. Fukui, M. Nakayama and T. Horie, *J. Sci. Hiroshima Univ.*, A-II, **33**, 305 (1969).

*2 This paper was read before the 22th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969. A part of this work has already been briefly communicated: *Experientia*, **25**, 355 (1969).

1) J. W. ApSimon, N. B. Haynes, K. Y. Sim and W. B. Whalley, *J. Chem. Soc.*, **1963**, 3780.

2) T. A. Geissman, R. Mukherjee and K. Y. Sim, *Phytochem.*, **6**, 1575 (1967).

3) W. Herz, C. M. Gast and P. S. Subramaniam, *J. Org. Chem.*, **33**, 2780 (1968).

4) F. Bohlmann and C. Zdero, *Tetrahedron Lett.*, **1967**, 3239.

5) C. H. Brieskorn and H. Michel, *ibid.*, **1968**, 3447.

6) N. R. Krishnaswamy, T. R. Seshadri and P. J. Tahir, *Indian J. Chem.*, **6**, 676 (1968).

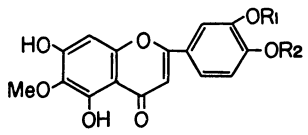
*3 Pedalitin (from *Sesanum indicum*) was identified as 6-methoxy-5,7,3′,4′-tetrahydroxyflavone (N. Morita, *Chem. Pharm. Bull.* (Tokyo), **8**, 59, 66 (1960)). However, the revised structure has been postulated to be 7-methoxy-5,6,3′,4′-tetrahydroxyflavone by two groups of researchers (N. R. Krishnaswamy *et al.*[6] and K. Fukui, M. Nakayama, T. Matsui, M. Masumura and T. Horie, *Nippon Kagaku Zasshi*, **90**, 1270 (1969)).

7) K. Fukui, M. Nakayama and T. Horie, This Bulletin, **42**, 2327 (1969).

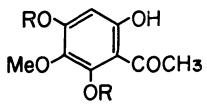
8) P. S. Phadke, A. V. Rama Rao and K. Venkataraman, *Indian J. Chem.*, **5**, 131 (1967).

9) W. Baker, *J. Chem. Soc.*, **1933**, 1381; K. Venkataraman and H. S. Mahal, *ibid.*, **1934**, 1767.

*4 The NMR spectra in this paper were measured with a Hitachi R-20 spectrometer (60 MHz), using tetramethylsilane as the internal standard (δ-value in $CDCl_3$); s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

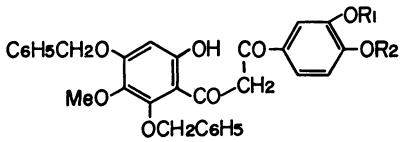


I

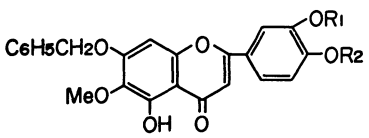


II R=$CH_2C_6H_5$

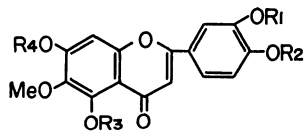
VII R=Et



III



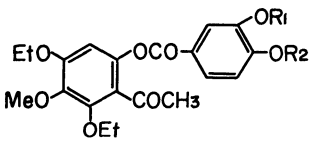
IV



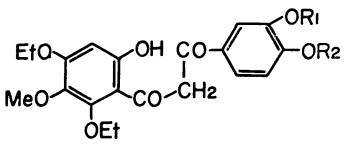
V R3=R4=Ac

VI R3=R4=Et

X R3=H, R4=Et



VIII



IX

I	III, IV	V	VI, VIII, IX, X
a R_1=Me, R_2=H	a R_1=Me, R_2=$CH_2C_6H_5$	a R_1=Me, R_2=Ac	a R_1=Me, R_2=Et
b R_1=H, R_2=Me	b R_1=$CH_2C_6H_5$, R_2=Me	b R_1=Ac, R_2=Me	b R_1=Et, R_2=Me
c R_1=R_2=H	c R_1=R_2=$CH_2C_6H_5$	c R_1=R_2=Ac	c R_1=R_2=Et

Table 1.*[4] NMR Data of benzyloxyflavones (IVa-c)

	IVa	IVb	IVc
OH	12.78_s	12.87_s	12.87_s
Arom. H			
C-3) or C-8)	6.57_s (2H)	6.53_s 6.57_s	6.56_s 6.60_s
C-5′	6.96_d J=9.0 Hz	7.01_d J=9.0 Hz	6.97_d J=9.0 Hz
others	$7.20—7.60_m$(12H)	$7.30—7.65_m$(12H)	$7.20—7.60_m$(17H)
$C_6H_5CH_2O$	5.25_s(4H)	5.27_s(4H)	5.30_s(6H)
CH_3O	3.97_s(3H) 3.94_s(3H)	3.97_s(6H)	3.97_s(3H)

sodium acetate and by the subsequent partial debenzylation. The flavones, IVa-c, can thus be formulated as 7-benzyloxy-5-hydroxy-6-methoxyflavone derivatives. The catalytic hydrogenolysis of IVa-c over palladium charcoal gave the desired flavones (Ia-c), which were then converted into the corresponding acetates (Va-c) by the conventional method. The hydroxyflavones (Ia, b) gave the corresponding ethyl ether derivatives (VIa, b) upon complete ethylation with diethyl sulfate and anhydrous potassium carbonate.

In order to establish the structure of the hydroxyflavones (Ia-c), the ethyl ether derivatives (VIb, c) were prepared by the following unambiguous method. The esterification of 2,4-diethoxy-6-hydroxy-3-methoxyacetophenone (VII)[10] with 3-ethoxy-4-methoxy- or 3,4-diethoxy-benzoyl chloride yielded 6-(3-ethoxy-4-methoxybenzoyloxy)- (VIIIb) or 6-(3,4-diethoxy benzoyloxy)- (VIIIc) -2,4-di-

10) L. Farkas, L. Hörhammer, H. Wagner, H. Rösler and R. Gurniak, *Chem. Ber.*, **97**, 610 (1964).

ethoxy-5-methoxyacetophenone. The esters (VIIIb and VIIIc) gave 6,4′-dimethoxy-5,7,3′-triethoxy-(VIb) and 6-methoxy-5,7,3′,4′-tetraethoxy-(VIc)-flavone *via* the corresponding diketones (IXb and IXc) by a method similar to that described above. These flavones (VIa, b) were identified by direct comparisons with the ethyl derivatives obtained by the ethylation of the hydroxy-flavones (Ia, b).*5 Furthermore, the partial ethylation of the hydroxy-flavones (Ib, c) gave the 5-hydroxyflavone derivatives (Xb, c), which were then easily converted into monoacetates. Xb, c were also prepared from VIb, c by partial deethylation with anhydrous aluminum chloride. The hydroxyflavones (Ia-c) were now established to be 5,7-dihydroxy-6-methoxy-flavone derivatives.

Ia and Va were shown to be identical with the natural pigment and its acetate*6 by a mixed-melting-point determination and by NMR, IR and UV spectral comparisons.*7

On the other hand, the natural desmethoxycentaureidin and 6-methoxyluteolin were, unfortunately, could not be compared directly, but the properties of the synthetic samples of Ib and Ic were superimposable upon those recorded in the literature.[4-6]

Experimental*8

ω-(4-Benzyloxy-3-methoxybenzoyl)-(IIIa), ω-(3-benzyloxy-4-methoxybenzoyl)- (IIIb), and ω-(3,4-dibenzyloxybenzoyl) - (IIIc) - 2,4 - dibenzyloxy-6-hydroxy-3-methoxyacetophenone. A mixture of the crude dibenzyloxyacetophenone (II)[7] (2—2.5 g) and 3,4-disubstituted benzoyl chloride (2.5—3.0 g) in anhydrous pyridine (8.0 m*l*) was heated at 120°C for 2 hr. The cooled reaction mixture was poured into diluted hydrochloric acid, and then extracted with ether (the insoluble material was filtered off). The ether layer was washed with a sodium carbonate solution and water. The removal of the solvent gave a semi-solid, which was then dried in a desiccator.

A mixture of the crude ester, freshly-powdered potassium hydroxide (2.5 g), and pyridine (15—20 m*l*) was heated at 60°C for 4 hr with stirring. The reaction mixture was acidified with diluted hydrochloric acid, and then extracted with ether. The ether layer was washed with a sodium carbonate solution. The solvent was evaporated to 2—5 m*l* and then allowed to stand overnight. The separated crystals were collected and recrystallized to give III (Table 2), which gave a green color with ferric chloride in ethanol.

7,4′-Dibenzyloxy-6,3′-dimethoxy- (IVa), 7,3′-dibenzyloxy-6,4′-dimethoxy- (IVb) and 7,3′,4-tribenzyloxy-6-methoxy- (IVc)-5-hydroxyflavone. A mixture of III (500—700 mg) and anhydrous sodium acetate (2—4 g) in acetic acid (20—40 m*l*) was heated at 140°C for 4—5 hr. The reaction mixture was then diluted with water and extracted with ether. The ether layer was washed with a sodium carbonate solution and then allowed to stand overnight in a refrigerator. The combined precipitates were crystallized to give IV (Table 3), which gave a dark brown or dark greenish brown color with ferric chloride in ethanol and a red color with magnesium and hydrochloric acid.

6,3′-Dimethoxy-5,7,4′-tribenzyloxyflavone (5-O-Benzylether of IVa). A mixture of IVa (30 mg), benzyl chloride (0.1 m*l*), and anhydrous potassium carbonate (300 mg) in dimethylformamide (1.0 m*l*) was gently refluxed for 2 hr. The cooled reaction mixture was diluted with water and then extracted with ether. The ether layer was washed with diluted hydrochloric acid and water, and then subjected to evaporation under a vacuum. The oily residue was triturated with hexane and then treated with ether at 20—30°C. The separated crystals were recrystallized from methanol to give tribenzyloxyflavone as colorless needles; mp 127°C (115—116°C sinter); yield, 25 mg (71%). IR: 1638 cm^{-1} ($CHCl_3$). UV: λ_{max} mμ (log ε); 240_{sh}*9 (4.40), 264 (4.20), 330 (4.47).

Found: C, 76.05; H, 5.30%. Calcd for $C_{38}H_{32}O_7$: C, 75.98; H, 5.37%.

6,3′-Dimethoxy-5,7,4′-trihydroxyflavone (Ia), 6,4′-dimethoxy-5,7,3′-trihydroxyflavone (desmethoxycentaureidin) (Ib) and 6-methoxy-5,7,3′,4′-tetrahydroxyflavone (6-methoxyluteolin) (Ic). A solution of IV (350—400 mg) dissolved in a mixture of methanol and ethyl acetate (1:2: 80—100 m*l*) was shaken with palladium charcoal (10%: 200 mg) in an atmosphere of hydrogen for 3—4 hr. After the catalyst had been filtered, the filtrate was evaporated and the residue was recrystallized to give I (Table 4), which gave a dark brown or dark greenish brown color with ferric chloride in ethanol.

Ia was identified with a natural pigment*6 by a mixed-melting-point determination and by IR and UV spectral comparisons.

Acetates (Va-c) of I were synthesized by a hot acetic anhydride-pyridine method (Table 5). The NMR spectra of V were assigned as is shown in Table 6.

Va was found to be identical with the triacetate of the natural pigment by a mixed-melting-point determination and by NMR, IR, and UV spectral comparisons.

6-(3-Ethoxy-4-methoxybenzoyloxy)-(VIIIb) and 6-(3,4 - diethoxybenzoyloxy) - (VIIIc) - 2,4 - diethoxy-3-methoxyacetophenone. A mixture of VII[10] (2.0 g) and 3-ethoxy-4-methoxybenzoyl chloride (2.0 g) (or 3,4-diethoxybenzoyl chloride (2.1 g)) in anhydrous pyridine (5.0 g) was heated at 120°C for 2 hr. The reaction mixture was then treated by the usual method, and the crude product was recrystallized (Table 7).

ω-(3-Ethoxy-4-methoxybenzoyl)- (IXb) and ω-(3,4-diethoxybenzoyl)- (IXc)-2,4-diethoxy-6-hydroxy-3-methoxy-acetophenone. A mixture of VIII (1.5 g) and freshly-powdered potassium hydroxide (3.0 g) in anhydrous pyridine (15 g) was heated at 60°C for 4 hr with stirring. The reaction mixture was then treated by the method described in the case of III, and the crude

*5 The synthesis of VIa was previously reported by the present authors (T. Horie, M. Masumura, K. Fukui and M. Nakayama, This Bulletin, **41**, 1460 (1968)).

*6 The natural pigment was kindly supplied by Professor W. B. Whalley, University of London.

*7 Recently, Ia has also been synthesized from 3-methoxy-2,4,6-trihydroxyacetophenone by Drs. K. Y. Sim and R. Mukherjee (private communications).

*8 All the melting points are uncorrected; the UV spectra were measured in ethanol.

*9 sh=shoulder.

Table 2. ω-(3,4-Disubstituted benzoyl)-2,4-dibenzyloxy-6-hydroxy-3-methoxyacetophenones (IIIa-c)

Compounds	Mp (°C) (From solvent)[a]	Cryst. form	Yield (%)	Formula	Found C%	Found H%	Calcd C%	Calcd H%
IIIa	124.5—125.5 (EA-E)	Yellow needles	9.5	$C_{38}H_{34}O_8$	73.90	5.40	73.77	5.54
IIIb	183—184 (MEK)	Yellow prisms	11	$C_{38}H_{34}O_8$	73.69	5.59	73.77	5.54
IIIc	136.5—137.5 (EA)	Yellow prisms	10	$C_{44}H_{38}O_8$	76.26	5.47	76.06	5.51
	135.5 (125 sinter) (E)	Yellow needles						

a) EA=Ethyl acetate, E=Ethanol, MEK=Methyl ethyl ketone.

Table 3. 7-Benzyloxy-5-hydroxy-6-methoxyflavones (IVa-c)

Compounds	Mp (°C) Cryst. form (From solvent)[a]	Yield (%)	IR (C=O) cm^{-1} (Nujol)	UV λ_{max} mμ (log ε) EtOH	UV λ_{max} mμ (log ε) EtOH-$AlCl_3$	Formula	Found C% H%	Calcd C% H%
IVa	166—167.5	71	1658	243.5(4.26)	260 (4.16)	$C_{31}H_{26}O_7$	72.73	72.93
	Colorless needles		1624	277.5(4.26)	292 (4.26)		5.35	5.13
	(E)			340 (4.42)	364 (4.41)			
IVb	145—146.5	71	1658	243.5(4.29)	261 (4.16)	$C_{31}H_{26}O_7$	72.84	72.93
	Pale yellow		1640	277 (4.24)	293 (4.25)		5.20	5.13
	needles (E)			339 (4.39)	364 (4.38)			
IVc	158—159 (143—145 sinter)	78	1655 (broad)	242.5(4.32)	258.5(4.21)	$C_{37}H_{30}O_7$	75.98	75.75
				277.5(4.25)	295 (4.28)		5.24	5.16
	Colorless needles			337 (4.43)	360 (4.38)			
	(E)							

a) E=Ethanol.

Table 4. 5,7-Dihydroxy-6-methoxyflavones (Ia-c)

Compounds	Mp (°C) Cryst. form (From solvent)[a]	Yield (%)	IR cm^{-1}	UV λ_{max} mμ (log ε) EtOH	UV λ_{max} mμ (log ε) EtOH-$AlCl_3$	Formula	Found C% H%	Calcd C% H%
Ia (Syn.)	226—227	82	3400, 1666[b]	275(4.19)	260 (4.12)	$C_{17}H_{14}O_7$	61.95	61.82
	Yellow needles		3200, 1624	346(4.41)	286 (4.18)		4.13	4.27
	(aq. E)		3100		370 (4.41)			
(Nat.)	226—227		3400, 1663[b]	275(4.20)	260 (4.14)			
	Yellow needles		3150, 1620	346(4.42)	286.5(4.20)			
	(aq. E)		3100		370 (4.42)			
Ib	262—263	83	3390(broad)[c]	245(4.24)	261.5(4.19)	$C_{17}H_{14}O_7$	61.56	61.82
	Yellow needles		1650	275(4.23)	289 (4.14)		4.05	4.27
	(E)		1615	344(4.40)	367 (4.39)			
(Lit.)[4]	269—272		3430(broad)					
			1670	273				
			1630	342	370			
Ic	264—266	78	3380(broad)[c]	255(4.21)	279 (4.28)	$C_{16}H_{12}O_7$	60.75	60.76
	Yellow needles		1658	273(4.21)	400 (4.38)		3.80	3.82
	(aq. M)		1615	350(4.42)				
(Lit.)[5]	258—262		3390(broad)	256	284			
			1655	273	365			
			1600	348				

a) aq.=aqueous; E=Ethanol; M=Methanol. b) Nujol. c) KBr.

TABLE 5. ACETATES (Va-c) OF 5,7-DIHYDROXY-6-METHOXYFLAVONES (I)

Compounds	Mp (°C) Cryst. form (From solvent)[a]	Yield (%)	IR (C=O) cm^{-1} (Nujol)	UV λ_{max}^{EtOH} mμ (log ε)	Formula	Found C% H%	Calcd C% H%
Va (Syn.)	217—218	95	1765	241.5(4.27)	$C_{23}H_{20}O_{10}$	60.52	60.52
	Colorless needles		1643	264.5(4.26)		4.26	4.42
	(E)			316 (4.32)			
(Nat.)	217—218						
	Colorless needles		1765	242 (4.31)			
	(E)		1643	264.5(4.30)			
				316 (4.38)			
Vb	186.5—187	92	1775	262 (4.17)	$C_{23}H_{20}O_{10}$	60.38	60.52
	Colorless needles		1640	320 (3.93)		4.29	4.42
	(E)						
(Lit.)[4]	189—190			261			
				319			
Vc	202.5—203 (180 sinter)	85	1776	265 (4.37)	$C_{24}H_{20}O_{11}$	59.25	59.50
	Colorless needles		1647	302 (4.39)		4.44	4.16
	(E)						
(Lit.)[6]	170—171						

a) E=Ethanol.

TABLE 6. NMR DATA OF Va-c*4

	Va	Vb	Vc
Arom. H			
C-3	6.57_s	6.55_s	6.60_s
C-8	7.28_s	7.28_s	7.27_s
C-2′	7.38_{bs}	7.57_d J=2.5 Hz	7.72_d J=2.5 Hz
C-5′	7.13_d J=9.0 Hz	7.07_d J=9.0 Hz	7.36_d J=9.0 Hz
C-6′	7.46_q J=9.0, 2.5 Hz	7.75_q J=9.0, 2.5 Hz	7.76_q J=9.0, 2.5 Hz
CH_3CO	2.33_s	2.36_s	2.34_s (6H)
	2.38_s	2.39_s	2.39_s
	2.48_s	2.49_s	2.50_s
CH_3O	3.87_s	3.87_s	3.87_s
	3.90_s	3.91_s	

TABLE 7. 6-(3,4-DISUBSTITUTED BENZOYLOXY)- (VIIIb, c) AND ω-(3,4-DISUBSTITUTED BENZOYL-)-(IXb, c)-2,4-DIETHOXY-6-HYDROXY-3-METHOXYACETOPHENONE

Compounds	Mp (°C) (From solvent)[a]	Cryst. form	Yield (%)	Formula	Found C%	Found H%	Calcd C%	Calcd H%
VIIIb	106—107 (M)	Colorless plates	59	$C_{23}H_{28}O_8$	63.92	6.81	63.88	6.53
VIIIc	106—107.5 (E)	Colorless prisms	57	$C_{24}H_{30}O_8$	64.71	6.71	64.56	6.77
IXb	107.5—108 (M)	Yellow needles	58	$C_{23}H_{28}O_8$	64.00	6.49	63.88	6.53
IXc	106—107.5 (M)	Yellow needles	45	$C_{24}H_{30}O_8$	64.39	6.58	64.56	6.77

a) M=Methanol; E=Ethanol.

Table 8. Some of ethoxyflavone derivatives

Compounds	Mp (°C) (From solvent)[a]	Cryst. form	Yield (%)	Formula	Found C%	Found H%	Calcd C%	Calcd H%
VIa	172—173 (E)	Pale yellow prisms	50[b]	$C_{23}H_{26}O_7$	66.50	6.19	66.65	6.32
VIb	154—155 (E)	Colorless needles	52[b] 93[c]	$C_{23}H_{26}O_7$	66.63	6.46	66.65	6.32
VIc	142—143.5 (E)	Colorless prisms	93[c]	$C_{24}H_{28}O_7$	67.27	6.44	67.27	6.59
Xb	170—171 (E)	Pale yellow needles	62[b] 70[d]	$C_{21}H_{22}O_7$	65.23	5.79	65.27	5.74
Xc	152.5—153.5 (E)	Pale yellow needles	68[b] 45[d]	$C_{22}H_{24}O_7$	65.69	5.86	65.99	6.04
Acetate of Xb	165—166.5 (M)	Colorless plates	90	$C_{23}H_{24}O_8$	64.69	5.57	64.48	5.65
Acetate of Xc	172—173.5 (aq. M)	Colorless needles	92	$C_{24}H_{26}O_8$	65.15	5.92	65.09	5.90

a) E=Ethanol; M=Methanol; aq.=aqueous.
b) Yield from I. c) Yield from VIII. d) Yield from VI.

product was recrystallized (Table 7).

5,7-Diethoxy-6-methoxyflavone Derivatives (VIa–c).

a) From I. A mixture of I (20—30 mg), diethyl sulfate (0.2—0.3 m*l*), and anhydrous potassium carbonate (0.5—1.0 g) in anhydrous acetone (15—20 m*l*) was refluxed for 20—24 hr and then treated with aqueous methanol (10%: 15 m*l*). The solvent was distilled off. The resulting precipitate was collected and recrystallized to give VIa, b (Table 8).

b) From IX. Concentrated sulfuric acid (0.7 m*l*) was added to a solution of IX (700 mg) in acetic acid (7.0 m*l*) after which the mixture was heated at 70°C for 3 min. The reaction mixture was treated with hot water (30 m*l*), and then the separated precipitate was collected and washed with water. The recrystallization of the precipitate afforded VI, which was undepressed in melting point on admixture with the sample of a).

7-Ethoxy-5-hydroxy-6-methoxyflavone Derivatives (X).

a) From I. A mixture of I (30 mg), diethyl sulfate (0.2 m*l*), and anhydrous potassium carbonate (0.4 g) in acetone was refluxed for 6 hr and then treated by the method described in the case of VI. The crude product was recrystallized to give Xb, c (Table 8).

b) From VI. To a solution of VI (500 mg) in anhydrous nitrobenzene (6.0 g), a solution of anhydrous aluminum chloride (5.0 g) in absolute ether (15 m*l*) was added, and the mixture was heated at 47°C for 5 hr. After the mixture had been poured into 1% hydrochloric acid (250 m*l*), the solution was concentrated to 100 m*l* in a vacuum. The resulting precipitate was collected, washed with water, and recrystallized to give Xb, c; the melting point was undepressed on admixture with the sample of a).

Acetate of X. The acetate was prepared by a hot acetic anhydride-pyridine method (Table 8).

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