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CIRCULAR DICHROISM, OPTICAL ROTATORY DISPERSION AND ABSOLUTE CONFIGURATION OF FLAVANONES, 3-HYDROXYFLAVANONES AND THEIR GLYCOSIDES

DETERMINATION OF AGLYCONE CHIRALITY IN FLAVANONE GLYCOSIDES*

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Abstract—Flavanones of 2*S* configuration and 3-hydroxyflavanones of 2*R*,3*R* configuration, having equatorial 2-aryl substituents in the former or diequatorial 2,3-substituents in the latter, exhibit a positive Cotton effect due to the $n \rightarrow \pi^*$ transition (~ 330 nm) and a negative Cotton effect in the $\pi \rightarrow \pi^*$ region (~ 280–290 nm). Flavanone glycosides possessing chiral aglycones show Cotton effects quite similar to their optically active aglycones while flavanone glycosides having racemic aglycones show only weak Cotton effects at 250–350 nm. The $\pi \rightarrow \pi^*$ Cotton effect is more suitable for determining aglycone chirality in flavanone glycosides. In addition to the two high wavelength bands, 2*S*-flavanones generally showed a positive Cotton effect at 245–270 nm and a negative Cotton effect at 225–240 nm. *trans* 2*R*,3*R*-3-Hydroxyflavanones gave two Cotton effects below 270 nm both of which were positive.

CHEMICAL and spectroscopic studies have defined[1] the relative and absolute configuration of many optically active flavonoids. An ORD and CD study has been initiated in order to establish the absolute configuration of flavonoids of unknown stereochemistry and to provide more definitive information than is available from single wavelength measurements. We find that the absolute configuration of flavanones, 3-hydroxyflavanones and their glycosides can be determined by ORD or CD, in conjunction with NMR data, from milligram quantities of material.

Flavanones and 3-hydroxyflavanones show[2] a UV maximum at 270–290 nm and an inflection at 320–330 nm. These UV absorptions have been assigned[3] $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ origins, respectively. Snatzke has derived[4a] a relationship between the chirality of α,β-unsaturated ketones and the sign of their high wavelength Cotton effects. Extension[4b] of this rule to aryl ketones has shown that flavanones of configuration I will exhibit a positive Cotton effect at the $n \rightarrow \pi^*$ absorption band. Rules have also been suggested[5] for correlation of —C═C—C═O absolute conformation with the sign of the $\pi \rightarrow \pi^*$ Cotton effect but Dreiding models of isomeric flavanones do not point definitely to either chirality.

Examination of the ORD and CD of flavanones of known absolute configuration showed positive Cotton effects at high wavelength for (−)-hesperetin (IIa), (−)-

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liquiritigenin (IIb) and (−)-eriodictyol (IIc) and a negative Cotton effect for (+)-sakuranetin (IId). Application of the modified octant rule[4] for α,β-unsaturated ketones to these flavanones, having equatorial 2-aryl substituents, predicts the first three to be of 2*S* configuration and the last to be 2*R*, in agreement with structural determination.[6, 7] The ORD and CD of the 3-hydroxyflavanones (+)-dihydroquercetin (IIIa) and (+)-dihydrorobinetin (IIIb) showed positive Cotton effects and (−)-dihydrofisetin (IIIc) a negative Cotton effect centered in the region of n → π* absorption. With the 2,3-substituents diequatorial, the modified octant rule[4] predicts configuration 2*R*,3*R* for the first two and 2*S*,3*S* for the latter. The CD and ORD results are in agreement with absolute configurations assigned to these three 3-hydroxyflavanones by chemical methods.[7a, 8, 9]

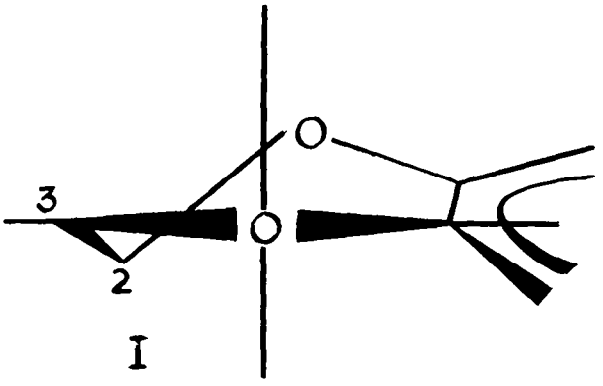
Therefore, examination of the CD and ORD of flavanones and 3-hydroxyflavanones of known configuration has led to the following conclusions. Flavanones of 2*S* configuration and 3-hydroxyflavanones of 2*R*,3*R* configuration, having the 2-aryl group substituted equatorially to the heterocyclic ring in the former or having the 2,3-groups substituted diequatorially in the latter, exhibit a positive Cotton effect due to the n → π* transition and a negative Cotton effect in the π → π* region.

It was of interest to determine the absolute configuration of two samples of naringenin (IIe), one of which was dextrorotatory and one of which was levorotatory, which had been obtained by enzymic hydrolysis of two samples of naringin (IIf), a bitter flavanone glycoside present in grapefruit. Both naringin samples were levorotatory,* one of commercial origin and one having been isolated from grapefruit. In view of the high value of the coupling constant ($J_{2,3}$) between protons in the 2 and 3 position of the heterocyclic ring, it has been concluded[10a] that all natural flavanones and 3-hydroxyflavanones exist in the thermodynamically favoured conformation with the 2 or 2,3-substituents equatorial. Since the 2-aryl group of both (+)-naringenin and (−)-naringenin is equatorial ($J_{2,3a}$ = 12·5 Hz),[10b] the negative Cotton effect we observed near 325 nm allows assignment of configuration *R* at C-2 in (+)-naringenin and the positive Cotton effect we found for (−)-naringenin establishes configuration 2*S*.

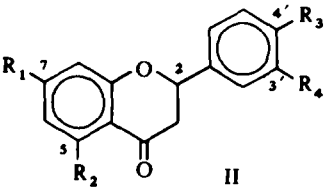
Table 1 contains CD data[11a] for a wide variety of optically active flavanones and 3-hydroxyflavanones. With the exception of the flavanone sakuranetin and the 3-hydroxyflavanone dihydrofisetin, in which cases both isomers have been found to occur naturally, all of the flavanones studied are 2*S* and all 3-hydroxyflavanones examined are 2*R*,3*R*. ORD data are listed[11b] in the Experimental.

Since a flavanone or 3-hydroxyflavanone glycoside will exhibit optical activity due to the carbohydrate moiety in addition to the chiral centres of the aglycone, we have examined the ORD and CD of compounds in which the aglycones are optically active in one case and racemic in another. Direct CD measurements on naturally occurring flavanone glycosides should provide information concerning the chirality present in the aglycone. Small quantities of natural material could then be studied without resorting to enzymic or chemical hydrolysis. Possible racemization during hydrolysis would be avoided. Aglycones (−)-naringenin (IIe) and (−)-hesperetin

* The commercial (−)-naringin was of unknown origin from Calbiochem, Los Angeles, California and had $[\alpha]_D^{27}$ −84·4 (50% acetone–water). The natural (−)-naringin was isolated from ¾ in Marsh Seedless grapefruit by Dr. R. M. Horowitz, Fruit and Vegetable Chemistry Laboratory, Pasadena, California $[\alpha]_D^{27}$ −95·1° (MeOH).



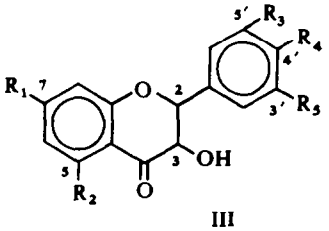
I



II

	R_1	R_2	R_3	R_4
a	—OH	OH	OCH_3	OH
b	—OH	H	OH	H
c	—OH	OH	OH	OH
d	$—OCH_3$	OH	OH	H
e	—OH	OH	OH	H
f	—Z	OH	OH	H
g	—Y	OH	OCH_3	OH
h	—OH	H	X	H

X = β-D-glucosyl-O-
Y = 6-O-α-L-rhamnosyl-β-D-glucosyl-O-
Z = 2-O-α-L-rhamnosyl-β-D-glucosyl-O-



III

	R_1	R_2	R_3	R_4	R_5
a	—OH	OH	OH	OH	H
b	—OH	H	OH	OH	OH
c	—OH	H	OH	OH	H

(IIa) were obtained by hydrolysis of their respective glycosides, (−)-naringin (IIf) and (−)-hesperidin (IIg). As shown in Figs 1 and 2, the Cotton effects of both glycosides are similar to those of the corresponding aglycones, confirming the 2*S* configuration of the aglycones in the flavanone glycosides. Two other examples were studied which have been configurationally established by independent methods, liquiritigenin[6] and dihydroquercetin.[7a] While our samples of (−)-liquiritigenin (IIb) and (−)-liquiritin (IIh) were obtained independently, the similar nature of their Cotton effects (Table 2) allows assignment of configuration 2*S* to (−)-liquiritin. Samples of (−)-astilbin (3,3′,4′,5,7-pentahydroxyflavanone-3-α-L-rhamnoside) and (+)-dihydroquercetin (IIIa) also were isolated separately but the nearly identical Cotton effects shown by these compounds allows the 2*R*,3*R* assignment to the aglycone portion of (−)-astilbin. Both 2*S* and 2*R*-naringin were levorotatory at the sodium D line but examination of the Cotton effect region by either ORD[11b] or CD showed the two diastereoisomers to have enantiomeric aglycones (*vide supra*).

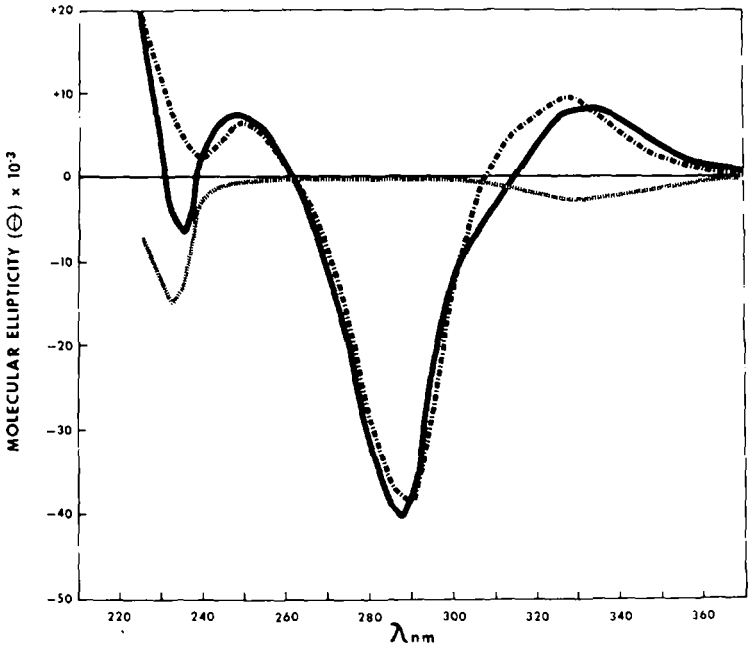


FIG. 1. CD curves. ——— Naringin ex immature $\frac{3}{4}$ in. Marsh Seedless grapefruit (R. M. Horowitz). ····· Naringin synthesized from naringin chalcone. —·—·— Naringenin from natural naringin by enzymic hydrolysis (R. M. Horowitz).

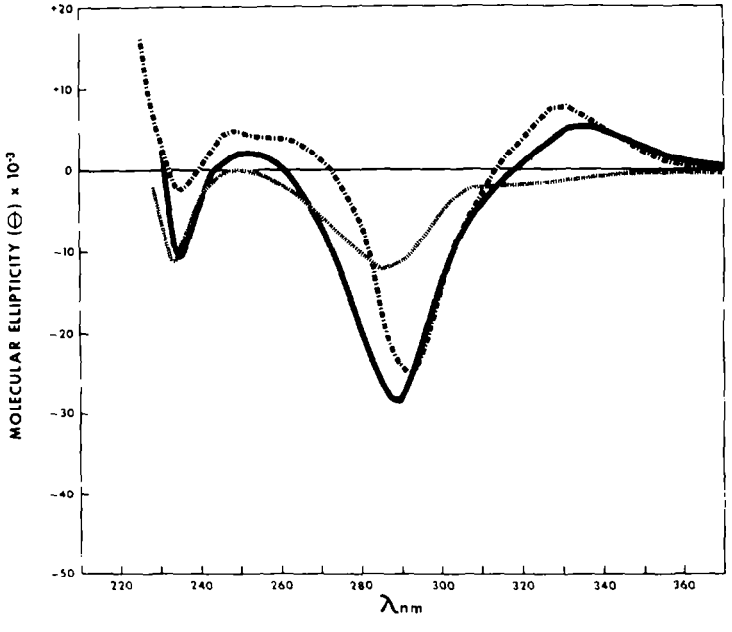


FIG. 2. CD curves. ——— Hesperidin (natural). ····· Hesperidin synthesized from hesperidin chalcone. —·—·— Hesperetin from natural hesperidin by acidic hydrolysis (H. R. Arthur, W. H. Hui, C. N. Ma, *J. Chem. Soc.* 632, 1956).

Chemical cyclization[12] of naringin chalcone gave 2*R*,2*S*-naringin in which the asymmetric C-2 of the aglycone was racemic. Enzymic hydrolysis of synthetic naringin gave optically inactive naringenin showing that there was no asymmetric induction upon chalcone cyclization or product isolation. The synthetic naringin still possessed substantial optical activity[12] due to the carbohydrate. Examination of the CD (Fig 1) of 2*R*,2*S*-naringin showed marked changes in comparison to (+) or (−)-naringenin and (−)-2*S*-naringin. While Cotton effects were still present in the 250–350 nm region, they were greatly reduced in magnitude and are probably related to asymmetric perturbation of the benzene ring chromophore by the optically active carbon atoms of the carbohydrate portion of the molecule. In a similar manner, hesperidin chalcone was cyclized[12] at pH 6 to form synthetic hesperidin. The synthetic hesperidin gave a CD (Fig 2) in which the large Cotton effects due to an α,β-unsaturated ketone located in an asymmetric environment were not as evident as they were in natural hesperidin and in the aglycone hesperetin (Fig 2). A Cotton effect near 290 nm suggested some residual optical activity in the aglycone of synthetic hesperidin. Due to hesperidin's water insolubility it was not possible to enzymically hydrolyze the synthetic hesperidin in order to determine the optical purity of the aglycone. From the above results, it is apparent that examination of the Cotton effect region of flavanone glycosides is diagnostic of the optical activity of the aglycone portion of the molecule since the natural flavanone glycosides show ORD and CD curves quite similar to those of their corresponding optically active aglycones while synthetic flavanone glycosides have smaller Cotton effects at 250–350 nm and yield racemic aglycones upon enzymic hydrolysis.

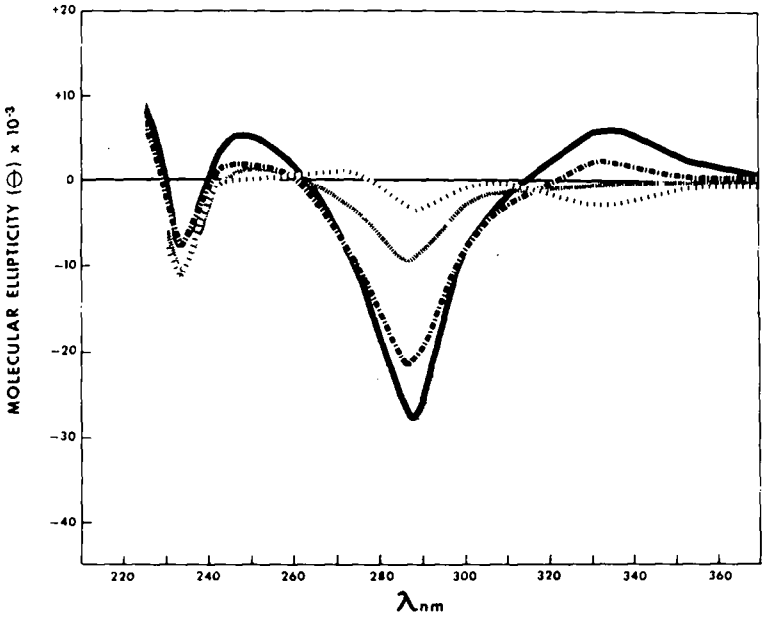


FIG 3. CD curves of naringin samples of varying optical purity.

87·5% 2*S*, 12·5% 2*R*. 75% 2*S*, 25% 2*R*.
62·5% 2*S*, 37·5% 2*R*. 55% 2*S*, 45% 2*R*.

Fig 3 shows CD curves of naringin (IIf) with varying amounts of 2*S* content. These mixtures were prepared from 2*S* and 2*R*,2*S*-naringin (Fig 1). Obviously, racemization of the aglycone leads to a proportional diminishing of the $\pi \rightarrow \pi^*$ Cotton effect near 290 nm. This band shows a molecular ellipticity of about $-40{,}000$ for 2*S* naringin and is essentially absent from the CD curve of 2*R*,2*S*-naringin (Fig 1). The positive $n \rightarrow \pi^*$ Cotton effect near 330 nm in the 2*S* sample also diminishes from $[\theta] \cong +10{,}000$ to near zero molecular ellipticity for 25% 2*S*-naringin (i.e. 62·5% 2*S*; 37·5% 2*R*). Further lessening of 2*S* character results in a negative CD band near 330 nm (Fig 3). Therefore the $\pi \rightarrow \pi^*$ Cotton effect appears more suitable for determining aglycone chirality in flavanone glycosides.

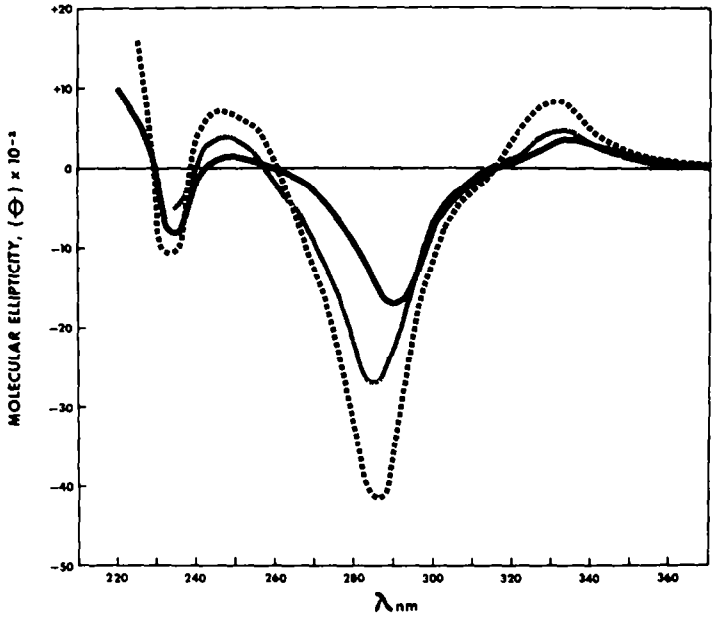


FIG. 4. CD curves of natural neohesperidosides and rutinosides. ——— Neohesperidin (natural from Mann Labs.). - - - - - - Poncirin ex *Poncirus trifoliata* (S. Hattori). ····· Isosakuranetin-7-rutinoside ex *Monarda didyma* (C. H. Brieskorn).

Other neohesperidosides (2-O-α-rhamnosyl-β-D-glucoside; IV) and one rutinoside (6-O-α-L-rhamnosyl-β-D-glucoside; V) were examined by CD. Fig 4 shows CD data for naturally occurring neohesperidosides (IVa, b) and rutinoside V. All three natural glycosides showed appreciable 2*S* content. Fig 5 shows CD data for synthetic neohesperidosides (IVa–e). Our sample of synthetic neohesperidin (IVa) (Fig 5) had more 2*S* content than a natural neohesperidin sample (Fig 4). This may be due either to racemization of C-2 during isolation of the natural material or to fractional recrystallization of synthetic IVa resulting in purification of the 2*S* diastereoisomer. The synthetic form of poncirin (IVb) (Fig 5) was similar to the natural isomer (Fig 4) inasmuch as both forms showed appreciable 2*S* configuration. About 25% of 2*S* chirality was present in the synthetic pinocembrin derivative (IVc) (Fig 5) (unsubstituted 4′-position) and a slight excess (~10%) of 2*S* isomer was detected in the 5,7-

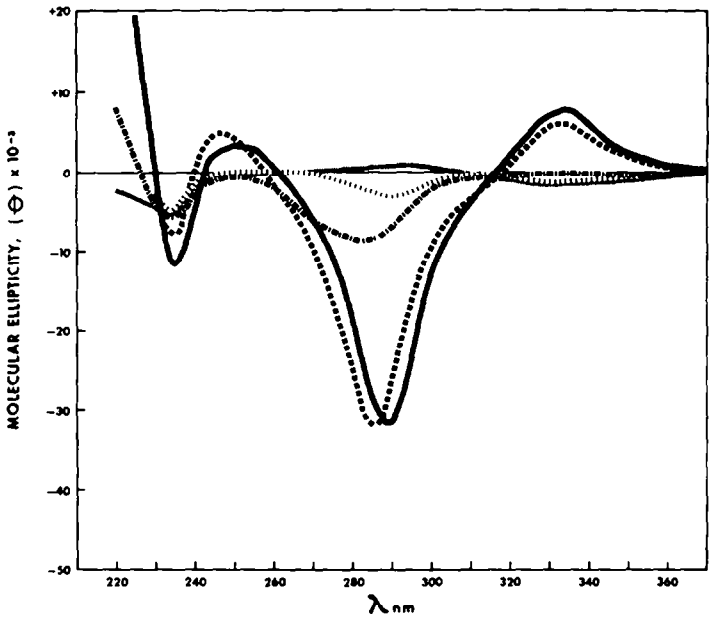
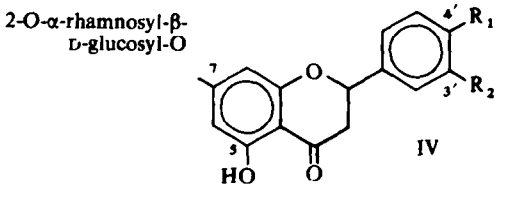


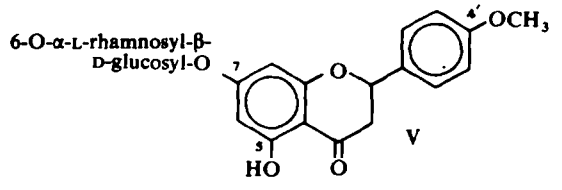
FIG 5. CD curves of synthetic neophesperidosides. ——— Neohesperidin (synthesized from phloracetophenone neohesperidoside with isovanillin, R. M. Horowitz). — — — Poncirin (synthesized by methylation of naringin, R. M. Horowitz). ····· Eriodictyol-7-neohesperidoside (synthetic – J. Chopin). — · — · — Pinocembrin-7-neohesperidoside (synthetic – J. Chopin). ····· 5,7-Dihydroxy-3',4'-dimethoxyflavanone-7-neohesperidoside (synthetic – J. Chopin). These last three compounds are described in J. Chopin and G. Dellamonica, *C. R. Acad. Sci., Paris* Ser. C. **262**, 1712 (1966).

dihydroxy-3',4'-dimethoxy flavanone-7-neohesperidoside (IVd) (Fig 5). The synthetic eriodictyol derivative (IVe) (Fig 5) (4'-hydroxyl group) appeared to be 2*R*,2*S*. In contrast to the naringin which was isolated from immature grapefruit using mild conditions (Experimental) and which gave a CD curve (Fig 1) indicative of 2*S* configuration, most commercial samples of naringin (IIf) gave a CD curve similar to that of the synthetic naringin curve shown in Fig 1. Therefore this 4'-OH compound (IIf) was usually obtained in the 2*R*,2*S* configuration.



IV

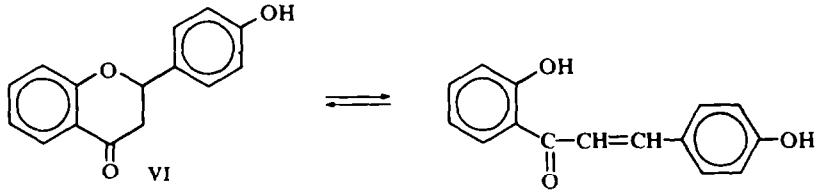
	R_1	R_2
a	$-OCH_3$	OH
b	$-OCH_3$	H
c	—H	H
d	$-OCH_3$	OCH_3
e	—OH	OH



V

The CD properties of additional flavanone glycosides are summarized in Table 2.

The above results emphasize the critical nature of the 4'-substituent upon the CD of flavanone glycosides. Since 4'-hydroxyflavanones containing a blocked 7-OH group are known to easily undergo the flavanone-chalcone interconversion (VI–VII),[13] optically active 4'-hydroxyflavanones containing a blocked 7-OH group would be



very susceptible to racemization. Possibly some 4'-OH compounds which are found to be 2*R*,2*S* occur naturally in a chiral form but are racemized either during extraction or purification. When proper precautions are taken during extraction and purification, CD can yield meaningful results about the stereochemistry of naturally occurring flavanone glycosides. Our results also show that a synthetic flavanone glycoside (not bearing a 4'-OH) may be enriched[14] in one isomeric form by fractional crystallization. The less soluble diastereoisomer obtained is of the natural configuration 2*S*. The possibility also exists that flavanone glycosides not possessing a 4'-OH may be formed stereospecifically[15] by chalcone cyclization.

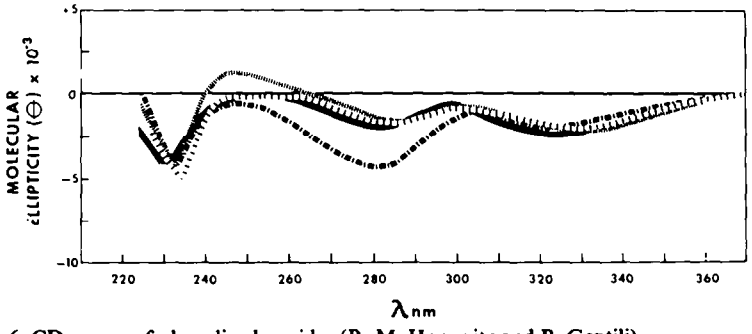
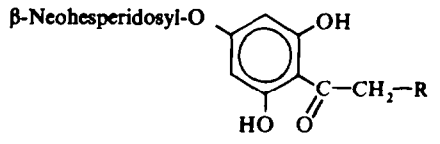
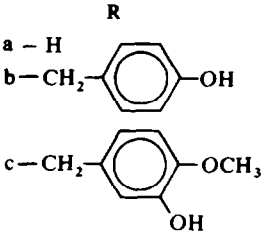


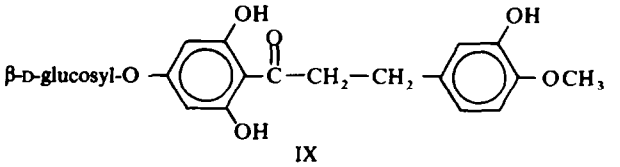
FIG 6. CD curves of phenolic glycosides (R. M. Horowitz and B. Gentili). ▬▬▬ Phloracetophenone-4-neohesperidoside. ▬ ▬ ▬ ▬ Hesperetin-7-glucoside dihydrochalcone. ▪▪▪▪▪▪▪▪▪▪▪▪▪▪ Naringin dihydrochalcone. ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ Neohesperidin dihydrochalcone.

In order to better understand the chiroptical properties of 2*R*,2*S*-flavanone glycosides some dihydrochalcone and acetophenone derivatives (VIII and IX) of carbohydrates were examined by CD. These compounds possessed a benzenoid chromophore system attached to the sugar but they did not have a C ring. As shown in Fig 6, all four phenolic glycosides had nearly identical Cotton effects near 325 nm and the three neohesperidosides (VIIIa–c) had similar Cotton effects near 280 nm while hesperetin-7-β-D-glucoside dihydrochalcone (IX) showed a negative Cotton effect twice as intense as VIIIa–c. Since these phenolic glucosides can have asymmetry only at the C atoms of the sugar, it is apparent that the presence of the sugar moiety



VIII





IX

is sufficient to induce optical activity in the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the acetophenone chromophore. The similarity of the CD curves of the phenolic glycosides to the CD curves of 2*R*,2*S* flavanone glycosides is further evidence for the presence of racemic aglycones in the latter compounds. All of the compounds included in this study have the carbohydrate linked to the phenolic chromophore through a *beta* linkage. Possibly *alpha* sugars would give rise to positive Cotton effects in the 220–350 nm region.*

While the entire discussion of the chiroptical properties of flavanones, 3-hydroxyflavanones, and their glycosides has so far been restricted to the $n \rightarrow \pi^*$ transition near 325 nm and the $\pi \rightarrow \pi^*$ transition near 290 nm, other absorption bands at lower wavelengths also gave rise to Cotton effects. It has been suggested[17] that all simple polyoxygenated 3-hydroxyflavanones and their 3-O-glycosides of *trans* 2*R*,3*R* configuration will show four Cotton effects in the order (+), (−), (+) and (+) from 400 to 220 nm. The first two bands are the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition respectively. The 3-hydroxyflavanones surveyed in this paper (Table 1) showed agreement with the above generalization[17] inasmuch as positive Cotton effects were observed at 245–270 nm and 225–240 nm for *trans* 2*R*,3*R* compounds. However, the configurationally related 2*S*-flavanones often gave four Cotton effects in the order (+), (−), (+) and (−) (Table 1) from high to low wavelength. The four bands are positioned in essentially the same wavelength regions for both flavanones and 3-hydroxyflavanones. It must be emphasized that the above behaviour for flavanones was noted in most cases but not all; that is, the sign of the fourth Cotton effect from the high wavelength end of the spectrum (~230 nm) was always positive for *trans*-2*R*,3*R*-3-hydroxyflavanones and usually negative for 2*S*-flavanones. The Cotton effects below 270 nm were generally weaker than the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ carbonyl Cotton effects and were therefore more susceptible to alterations in position and sign due to adjacent overlapping optically active absorption bands. Additional bands have been reported[18] at 200–240 nm in the CD of α,β-unsaturated ketones containing no other chromophore absorbing

* Cotton effects in unsubstituted phenyl glycosides have been reported.[16]

above 200 nm. Crabbé has noted[19] that the chromophore of the 3-hydroxyflavanones is quite complicated since the OH bearing center is located next to an acetophenone type system while the C-2 asymmetric center is *beta* to this chromophore but directly adjacent to a benzene ring. He states further[19] that orbital overlap between the two chromophores may form a *bis*-homoconjugated π-system which is quite complex electronically. The CD band observed near 230 nm for flavanones was fairly constant in sign and magnitude for natural and synthetic flavanone glycosides and for open chain phenolic glycosides. Therefore this band may be primarily due to an aromatic transition rather than a carbonyl band.

TABLE 1. CIRCULAR DICHROISM OF FLAVANONES AND 3-HYDROXYFLAVANONES

Compound	Conc. (%)	Circular dichroism data[a]	Source–Ref.
A. FLAVANONES			
5,6,7-Trihydroxy flavanone	0·065	$[\theta]_{345}$ +5260 (max); $[\theta]_{290}$ −27,800 (max); $[\theta]_{215}$ +32,400!	J. E. Watkin[b]
Pinocembrin (5,7-dihydroxy-)	0·029	$[\theta]_{325}$ +10,800 (max); $[\theta]_{285}$ −40,200 (max); $[\theta]_{240}$ −1410 (max); $[\theta]_{218}$ +54,800 (max); $[\theta]_{215}$ +39,300!	H. Erdtman[c]
Pinocembrin	0·027	$[\theta]_{327}$ +4340 (max); $[\theta]_{287}$ −16,400 (max); $[\theta]_{240}$ −1450 (max); $[\theta]_{220}$ +21,200 (max); $[\theta]_{208}$ +6260!	M. Hasegawa[d]
Pinocembrin	0·072	$[\theta]_{327}$ +6470 (max); $[\theta]_{287}$ −21,000 (max); $[\theta]_{240}$ −710 (max); $[\theta]_{220}$ +28,800!	E. Von Rudloff[e]
Pinocembrin	0·062	$[\theta]_{325}$ +13,100 (max); $[\theta]_{285}$ −50,800 (max); $[\theta]_{235}$ +2310!	
Matteucinol (5,7-dihydroxy-6,8-dimethyl-4′-methoxy-)	0·030	$[\theta]_{335}$ +6210 (max); $[\theta]_{313}$ +6210 (max); $[\theta]_{291}$ −35,800 (max); $[\theta]_{253}$ +4550 (max); $[\theta]_{240}$ −2070 (max); $[\theta]_{214}$ +38,300 (max); $[\theta]_{205}$ +8270!	Y. Tanabe
Dihydrowogonin (5,7-dihydroxy-8-methoxy-)	0·030	$[\theta]_{345}$ +2100 (max); $[\theta]_{310}$ +3820 (max); $[\theta]_{287}$ −15,300 (max); $[\theta]_{242}$ −1910 (max); $[\theta]_{221}$ +16,200 (max); $[\theta]_{210}$ +9540!	J. Chopin[g]
Dihydrowogonin	0·033	$[\theta]_{310}$ +10,400 (max); $[\theta]_{287}$ −42,100 (max); $[\theta]_{242}$ −4770 (max); $[\theta]_{220}$ +42,100 (max); $[\theta]_{215}$ +33,800!	H. Aft
Strobopinin (5,7-dihydroxy-8-methyl-)	0·020	$[\theta]_{330}$ +5410 (max); $[\theta]_{288}$ −25,000 (max); $[\theta]_{219}$ +27,000 (max); $[\theta]_{210}$ +14,900!	J. Chopin
Homoeriodictyol (5,7,4′-trihydroxy-3′-methoxy-)	0·024	$[\theta]_{330}$ +6050 (max); $[\theta]_{292}$ −30,900 (max); $[\theta]_{250-260}$ +2520 (max); $[\theta]_{240}$ −6300 (max); $[\theta]_{227}$ +13,900!	H. Aft
Eriodictyol (5,7,3′,4′-tetrahydroxy-)	0·064	$[\theta]_{327}$ +11,300 (max); $[\theta]_{293}$ −40,500 (max); $[\theta]_{253}$ +4960 (max); $[\theta]_{220}$ +36,900 (max); $[\theta]_{210}$ +13,100!	J. C. Pew[h]
Poriol (5,7,4′-trihydroxy-6-methyl-)	0·007	$[\theta]_{330}$ +7800 (max); $[\theta]_{290}$ −40,000 (max); $[\theta]_{253}$ +5300 (max); $[\theta]_{215}$ +37,000 (max); $[\theta]_{205}$ +10,600!	G. M. Barton[i]

TABLE 1—*continued*

Compound	Conc. (%)	Circular dichroism data[a]	Source-Ref.
Artocarpanone (5,2',4'-trihydroxy-7-methoxy-)	0·047	$[\theta]_{325}$ +520 (max); $[\theta]_{290-295}$ −1040 (max); $[\theta]_{275}$ +880 (max); $[\theta]_{235}$ −3380 (max); $[\theta]_{232}$ −1820!	K. Venkataraman[j]
Desmethoxymatteucinol (5,7-dihydroxy-6,8-dimethyl-)	0·060	$[\theta]_{340}$ +7580 (max); $[\theta]_{313}$ +8530 (max); $[\theta]_{292}$ −43,100 (max); $[\theta]_{238}$ −7100 (max); $[\theta]_{217}$ +38,400!	S. Sasaki[k]
Dihydrotectochrysin (5-hydroxy-7-methoxy-)	0·010	$[\theta]_{325-330}$ +2700 (max); $[\theta]_{285}$ −8110 (max); $[\theta]_{255}$0!	J. Chopin[l]
Perscicogenin (5,3'-dihydroxy-7,4'-dimethoxy-)	0·036	$[\theta]_{330}$ +4570 (max); $[\theta]_{290}$ −20,600 (max); $[\theta]_{250-255}$ +2640 (max); $[\theta]_{240}$ −3080 (max); $[\theta]_{220}$ +13,600!	W. Rahman[m]
Sakuranetin (5,4'-dihydroxy-7-methoxy-)	0·036	$[\theta]_{325}$ −3180 (max); $[\theta]_{285}$ +10,300 (max); $[\theta]_{235}$ −5960!	
Isosakuranetin (5,7-dihydroxy-4'-methoxy-)	0·041	$[\theta]_{325}$ +10,800 (max); $[\theta]_{287}$ −43,600 (max); $[\theta]_{250}$ +6630 (max); $[\theta]_{235}$ +6980!	M. Shimokoriyama[d]
Liquiritigenin (7,4'-dihydroxy-)	0·049	$[\theta]_{330}$ +17,100 (max); $[\theta]_{305}$ −28,200 (max); $[\theta]_{240}$ +12,400!	H. Aft
B. 3-HYDROXYFLAVANONES			
Dihydromyrecetin (5,7,3',4',5'-penta-hydroxy-)	0·063	$[\theta]_{330}$ +8130 (max); $[\theta]_{294}$ −25,400 (max); $[\theta]_{260-265}$ +9350 (max); $[\theta]_{243}$ −510 (max); $[\theta]_{227}$ +16,300!	R. Hansel[e]
Pinobanksin (5,7-dihydroxy-)	0·086	$[\theta]_{327}$ +8610 (max); $[\theta]_{292}$ −21,500 (max); $[\theta]_{222}$ +31,700 (max); $[\theta]_{217}$ +26,000!	E. Von Rudloff[e]
Pinobanksin	0·079	$[\theta]_{327}$ +9650 (max); $[\theta]_{287}$ −36,900 (max); $[\theta]_{245}$ +1380 (max); $[\theta]_{240}$ 0; $[\theta]_{220}$ +46,900!	H. Erdtman[p]
Dihydrofisetin (7,3',4'-trihydroxy-)	0·055	$[\theta]_{330}$ −7360 (max); $[\theta]_{305}$ +15,300 (max); $[\theta]_{270}$ −4470 (max); $[\theta]_{233}$ −10,500 (max); $[\theta]_{230}$ −7630!	"
Dihydrofisetin	0·058	$[\theta]_{330}$ −8280 (max); $[\theta]_{305}$ +22,900 (max); $[\theta]_{270}$ −4490 (max); $[\theta]_{240}$ −14,000 (max); $[\theta]_{230}$ −9980!	"
Silybin (see Ref q)	0·087	$[\theta]_{329}$ +11,100 (max); $[\theta]_{293}$ −42,700 (max); $[\theta]_{252}$ +6650 (max); $[\theta]_{225}$ +3210 (max); $[\theta]_{211}$ −5210 (max); $[\theta]_{208}$ 0!	H. Wagner[q]
Dihydrorobinetin (7,3',4',5'-tetra-hydroxy-)	0·063	$[\theta]_{332}$ +9850 (max); $[\theta]_{305}$ −24,400 (max); $[\theta]_{265-267}$ +7730 (max); $[\theta]_{235-237}$ +14,000 (max); $[\theta]_{222}$ +13,500!	"
Dihydroquercetin (5,7,3',4'-tetra-hydroxy-)	0·069	$[\theta]_{328-330}$ +6620 (max); $[\theta]_{295}$ −23,200 (max); $[\theta]_{255}$ +3970 (max); $[\theta]_{222}$ +22,500!	E. Von Rudloff[e]

TABLE 1—*continued*

Compound	Conc. (%)	Circular dichroism data[a]	Source–Ref.
Dihydroquercetin	0·046	$[\theta]_{328}$ +11,000 (max); $[\theta]_{295}$ −38,400 (max); $[\theta]_{256}$ +5950 (max); $[\theta]_{223}$ +36,400 (max); $[\theta]_{215}$ +16,100!	J. C. Pew[r]
Dihydroquercetin	0·037	$[\theta]_{325-330}$ +2470 (max); $[\theta]_{294}$ −7810 (max); $[\theta]_{260}$ +1810 (max); $[\theta]_{240}$ −1230 (max); $[\theta]_{223}$ +8720 (max); $[\theta]_{220}$ +5760!	C. W. Murray[s]
Dihydrokaempferol (5,7,4'-trihydroxy-)	0·094	$[\theta]_{327}$ +9810 (max); $[\theta]_{292}$ −35,600 (max); $[\theta]_{255}$ +7670 (max); $[\theta]_{237}$ +10,700 (max); $[\theta]_{232}$ +11,300!	W. E. Hillis[t]
Dihydrokaempferol	0·050	$[\theta]_{330}$ +9800 (max); $[\theta]_{290}$ −35,700 (max); $[\theta]_{255}$ +8070 (max); $[\theta]_{230}$ +11,200!	
7-Methyl-aromadendrin (5,4'-dihydroxy-7-methoxy-)	0·056	$[\theta]_{330}$ +11,500 (max); $[\theta]_{292}$ −37,800 (max); $[\theta]_{257}$ +9180 (max); $[\theta]_{235}$ +9010!	E. Ritchie[u]

! Last wavelength measured.

[a] All measurements were performed in methanol.

[b] J. E. Watkin, *Aspects Plant Phenolic Chem., Proc. Symp., 3rd, Univ. Toronto* 1963 39 (1964).

[c] ex *Pinus jeffreyi.*

[d] ex *Prunus verecunda* Koehne, M. Hasegawa and T. Shirato, *J. Am. Chem. Soc.* **79**, 450 (1957).

[e] ex Conifer heartwood.

[f] ex *Pinus banksiana.*

[g] ex *Prunus avium*, J. Chopin, D. Molho, H. Pachéco, C. Mentzer and G. Grenier, *Bull. Soc. Chim. France* 192 (1957).

[h] J. C. Pew, *J. Org. Chem.* **27**, 2935 (1962).

[i] ex (*Pseudotsuga menziesii* (Mirb.) Franco) roots infected with (*Poria weirii* Murr.), G. M. Barton, *Can. J. Chem.* **45**, 1020 (1967).

[j] ex *Artocarpus integrifolia*, K. G. Dave, S. A. Teland and K. Venkataraman, *J. Sci. Ind. Research (India)* **19B**, 470 (1960).

[k] ex *Matteucia orientalis*, S. Fujise and T. Kubota, *Chem. Ber.* **67**, 1905 (1934).

[l] ex *Prunus avium.*

[m] ex *Prunus Persica Batsch*, W. Rahman and S. P. Bhatnagar, *Aust. J. Chem.* **21**, 539 (1968).

[n] Commercial source.

[o] ex *Erythrophleum africanum*, R. Hänsel and J. Klaffenbach, *Arch. Pharm.* **294**, 158 (1961).

[p] ex *P. virginiana.*

[q] ex *Silybum marianum.* For structure see, A. Pelter and R. Hänsel, *Tetrahedron Letters* 2911 (1968).

[r] ex Douglas fir heartwood, J. C. Pew, *J. Am. Chem. Soc.* **70**, 3031 (1948).

[s] This is the sample having $[\alpha]_D$ +11 (50% acetone–water), which was discussed by J. C. Pew (*J. Org. Chem.* **27**, 2935 (1962)). This sample was found to be *trans*-2,3-dihydroquercetin by NMR analysis ($J_{2,3}$ 11 Hz).

[t] ex *Eucalyptus hemiphloia*, W. E. Hillis and A. Carle, *Aust. J. Chem.* **16**, 147 (1963).

[u] ex *Eucalyptus maculata*, R. J. Gell, J. T. Pinhey and E. Ritchie, *Aust. J. Chem.* **11**, 372 (1958).

TABLE 2. CIRCULAR DICHROISM OF FLAVANONE AND 3-HYDROXYFLAVANONE GLYCOSIDES

Compound	Conc. (%)	Circular dichroism data[a]	Source–Ref.
5,6,7-Trihydroxy flavanone glucuronide	0·043	$[\theta]_{355}$ +4390(max); $[\theta]_{285}$ −32,400(max); $[\theta]_{245}$ −10,500 (max); $[\theta]_{220}$ +18,300!	J. E. Watkin[b]
(±) Naringenin-5-β-D-glucoside	0·060	$[\theta]_{320-325}$ −1450 (max); $[\theta]_{285}$ +5080(max); $[\theta]_{235}$ −13,800 (max); $[\theta]_{215}$ −14,500 (max); $[\theta]_{205}$ −7250!	R. Häusel[c]
Phellamurin (5,7,4′-tetrahydroxy-8-(γ-hydroxyisovaleryl)-flavanonol-7 glucoside)	0·030	$[\theta]_{335}$ +3580(max); $[\theta]_{295}$ −32,200(max); $[\theta]_{245}$ −1800 (max); $[\theta]_{240}$ +5370 (max); $[\theta]_{230}$ −4480!	M. Hasegawa[d]
Hemiphloin (5,7,4′-trihydroxy-flavanone-6-β-D-glucoside)	0·076	$[\theta]_{330}$ +9430(max); $[\theta]_{290}$ −34,600(max); $[\theta]_{250}$ +5430 (max); $[\theta]_{235}$ +1430!	W. E. Hillis[e]
Neoponcirin (isosakuranetin-rhamnoglucoside)	0·055	$[\theta]_{330-335}$ +10,600 (max); $[\theta]_{285}$ −44,800 (max); $[\theta]_{245-250}$ +7080 (max); $[\theta]_{230}$ −8800!	M. Shimokoriyama[f]
Didymin (natural) (5,7-dihydroxy-4′-methoxy-flavanone-7-β-rhamnoglucoside)	0·051	$[\theta]_{330-335}$ +6990 (max); $[\theta]_{285}$ −45,500 (max); $[\theta]_{245}$ +6410 (max); $[\theta]_{235}$ −9320 (max); $[\theta]_{230}$ −4660!	H. Wagner[g]
Didymin (synthetic)	0·055	$[\theta]_{330}$ +5730(max); $[\theta]_{285}$ −37,500(max); $[\theta]_{245-250}$ +4860 (max); $[\theta]_{230}$ −8650!	H. Wagner
Isosakuranin (isosakuranetin-7-glucoside)	0·034	$[\theta]_{330}$ +9230(max); $[\theta]_{285}$ −46,200(max); $[\theta]_{245}$ +5930 (max); $[\theta]_{235}$ −8570 (max); $[\theta]_{225}$ +11,900!	M. Shimokoriyama
Isosakuranin	0·048	$[\theta]_{330}$ −4210 (max); $[\theta]_{280}$ +1600 (max); $[\theta]_{235}$ −10,800 (max); $[\theta]_{230}$ −7960!	M. Hasegawa[h]
Liquiritin (Liquiritigenin-4′-glucoside)	0·058	$[\theta]_{330}$ +11,900 (max); $[\theta]_{305}$ −19,800 (max); $[\theta]_{235}$ +13,000!	H. Aft
Liquiritin	0·038	$[\theta]_{330}$ +9440(max); $[\theta]_{300}$ −16,300(max); $[\theta]_{235}$ +12,600 (max); $[\theta]_{230}$ +7340!	M. Hasegawa
Dihydrokaempferol-7-rhamnoside	0·072	$[\theta]_{335}$ +8450(max); $[\theta]_{290}$ −38,600(max); $[\theta]_{225}$ +6640 (max); $[\theta]_{235}$ −3200!	R. G. Cooke[i]
Dihydroquercetin-3′-β-D-glucoside	0·031	$[\theta]_{327}$ +4510(max); $[\theta]_{290}$ −27,100(max); $[\theta]_{250}$ +4510 (max); $[\theta]_{220}$ +23,300!	H. L. Hergert
Dihydroquercetin-4′-glucoside	0·085	$[\theta]_{327}$ +11,000 (max); $[\theta]_{290}$ −37,900 (max); $[\theta]_{250}$ +6040 (max); $[\theta]_{225}$ +15,400!	L. Birkofer
Prunin (naringenin-7-glucoside)	0·047	$[\theta]_{335}$ +6100(max); $[\theta]_{285}$ −31,700(max); $[\theta]_{250}$ +4700 (max); $[\theta]_{235}$ −7460 (max); $[\theta]_{230}$ +5600!	M. Hasegawa
Prunin	0·076	$[\theta]_{332}$ +860 (max); $[\theta]_{285}$ −15,700 (max); $[\theta]_{250}$ +1490(max); $[\theta]_{235}$ −11,400(max); $[\theta]_{220}$ +4570!	R. M. Horowitz[j] and B. Gentili

TABLE 2—*continued*

Compound	Conc. (%)	Circular dichroism data[a]	Source–Ref.
Prunin	0·084	$[\theta]_{335}$ +4140 (max); $[\theta]_{285}$ −24,800 (max); $[\theta]_{250}$ +3620 (max); $[\theta]_{235}$ −9310 (max); $[\theta]_{220}$ +22,800!	R. M. Horowitz[k] and B. Gentili
Eriodictyol-7-glucoside acetate	0·043	$[\theta]_{322}$ −3930 (max); $[\theta]_{270}$ −7700 (max); $[\theta]_{228}$ −19,300 (max); $[\theta]_{220}$ −6840!	H. Wagner[j]
Homoeriodictyol-7-glucoside	0·067	$[\theta]_{340}$ +730 (max); $[\theta]_{287}$ −9800 (max); $[\theta]_{234}$ −7260 (max); $[\theta]_{225}$ +2540!	H. Wagner[j]
Sakuranin (sakuranetin-5-glucoside)	0·071	$[\theta]_{335}$ +11,100 (max); $[\theta]_{305}$ −18,700 (max); $[\theta]_{240}$ −12,000!	H. Aft
Hesperetin-7-β-glucoside	0·006	$[\theta]_{333}$ +7100 (max); $[\theta]_{290}$ −30,000 (max); $[\theta]_{250}$ +3250 (max); $[\theta]_{235}$ −6150 (max); $[\theta]_{230}$ +5060!	R. M. Horowitz[m] and B. Gentili
Hesperetin-7-β-glucoside	0·006	$[\theta]_{335}$ +600 (max); $[\theta]_{290}$ −10,500 (max); $[\theta]_{250}$ +970 (max); $[\theta]_{234}$ −7020 (max); $[\theta]_{230}$ −900!	R. M. Horowitz[n] and B. Gentili

! Last wavelength measured.

[a] All measurements were performed in methanol.

[b] ex *Scutellaria epilobifolia*, J. E. Watkin, *Aspects Plant Phenolic Chem., Proc. Symp., 3rd, Univ. Toronto*, 1963 39 (1964).

[c] ex *Helichrysin B*, R. Hänsel and D. Heise, *Arch. Pharm.* **292**, 398 (1959).

[d] ex *Phellodendron amurense*, M. Hasegawa and T. Shirato, *J. Am. Chem. Soc.* **75**, 5507 (1953).

[e] ex *Eucalyptus hemiphloria*, W. E. Hillis and A. Carle, *Aust. J. Chem.* **16**, 147 (1963). For structure see W. E. Hillis and D. H. S. Horn, *Aust. J. Chem.* **18**, 531 (1965).

[f] ex *Poncirus trifoliata*, M. Shimokoriyama, *Bot. Mag. Tokyo* **79**, 602 (1966).

[g] ex *Monarda didyma* L., H. Wagner, L. Hörhammer, G. Aurnhammer and L. Farkas, *Tetrahedron Letters* 1837 (1967).

[h] ex *Prunus verecunda* Koehne, M. Hasegawa and T. Shirato, *J. Am. Chem. Soc.* **79**, 450 (1957).

[i] ex *Exocarpus cupressiformis* Labill., R. G. Cooke and H. F. Haynes, *Aust. J. Chem.* **13**, 150 (1960).

[j] Prepared by partial acidic hydrolysis of naringin.

[k] Prepared by partial enzymic hydrolysis of naringin.

[l] Synthetic compound. L. Hörhammer, H. Wagner, H. Krämer and L. Farkas, *Tetrahedron Letters* 5133 (1966).

[m] Prepared by partial acidic hydrolysis of neohesperidin.

[n] Prepared by partial enzymic hydrolysis of neohesperidin.

EXPERIMENTAL

Preparation of flavanone glycosides containing racemic aglycones. Both naringin and hesperidin were prepared from their respective chalcones as reported.[12] The resulting flavanone glycosides were *not* recrystallized in order to avoid fractional recrystallization of diastereoisomers. Both 2*R*,2*S*-naringin and 2*R*,2*S*-hesperidin were characterized by m.p. data and IR and UV spectra in addition to paper chromatography. The 2*R*,2*S*-naringin was enzymatically hydrolyzed, in order to avoid acidic or basic conditions (Experimental procedure below), and the resultant naringenin was optically inactive as shown by ORD and CD measurements between 250–600 nm. The CD curves for these 2*R*,2*S*-flavanone glycosides are shown in Figs 1 and 2.

Enzymatic hydrolysis of 2R-*naringin* (IIf). (−)-2*R*-Naringin (Calbiochem—Lot No. 103145; 0·2247 g) and fungal hemicellulase (Nutritional Biochemical Corp. *via* R. M. Horowitz; 0·2035 g) were suspended in 300 ml 0·1 N acetate buffer at pH 4·63. The reaction mixture was stirred gently at ambient temp for 5 days. Fresh enzyme (40 mg) was added at 24 hr and 48 hr after the enzymatic hydrolysis was begun. At the end

of the 5-day period some precipitation had occurred but the pH was still near the initial value. The reaction mixture was filtered and the filtrate extracted with EtOAc (4 × 50 ml). After drying over $MgSO_4$, evaporation of the EtOAc extracts gave 0·0227 g pale yellow powder. This material was passed through a Sephadex LH-20 column, with MeOH as solvent, and upon removal of solvent (+)-2*R*-naringenin was obtained as shown by paper chromatography using 10% AcOH (5% $AlCl_3$ in 95% EtOH spray). The product (0·0087 g) had m.p. 250–251° and $[\alpha]_D^{27}$ +5·9° (acetone).

It should be mentioned that the above enzymatic hydrolysis has been successful only with the batch of enzyme obtained from Dr. Horowitz. Other samples of fungal hemicellulase, which actually appeared to be purer, did not hydrolyze naringin and only starting material was obtained even after prolonged reaction.

Isolation of (−)-2*S*-*naringin and preparation of* (−)-2*S*-*naringenin.* (−)-2*S*-Naringin was isolated from immature grapefruit by a procedure which carefully avoided racemizing conditions (R. M. Horowitz, unpublished observations). Dr. Horowitz then enzymatically hydrolyzed the naringin to (−)-2*S*-naringenin, $[\alpha]_D^{27}$ −22·5 (MeOH), by a procedure similar to one he has reported earlier.[20] The CD of 2*S*-naringin and 2*S*-naringenin are shown in Fig 1. Assuming Dr. Horowitz's samples to be essentially optically pure, it appears that the 2*R* samples of naringin and naringenin from the Calbiochem sample are about 27% optically pure (see also Ref 11b).

Optical rotatory dispersion and circular dichroism. ORD and CD spectra were obtained on a Cary 60 Spectropolarimeter equipped with a Cary 6001 CD accessory. ORD results are reported below.

A. *Flavanones*

2S-*Liquiritigenin* (IIb). ORD (*c*, 0·198, MeOH): $[\phi]_D$ −145, $[\phi]_{340}$ +2390 (pk), $[\phi]_{334}$ 0, $[\phi]_{318}$ −17,100 (tr), $[\phi]_{304}$ 0, $[\phi]_{287}$ +12,800 (pk), $[\phi]_{242}$ +20,500 (pk), $[\phi]_{230}$ +3420 (tr), $[\phi]_{220}$ +29,000!

2R-*Naringenin* (IIe). ORD (*c*, 0·185, MeOH): $[\phi]_{450}$ +13, $[\phi]_{413}$ 0, $[\phi]_{349}$ −1100 (tr), $[\phi]_{335}$ 0, $[\phi]_{298}$ +17,300 (pk), $[\phi]_{288}$ 0, $[\phi]_{271}$ −15,100 (tr), $[\phi]_{250}$ −9300!

2S-*Hesperetin* (IIa). ORD (*c*, 0·234, EtOH): $[\phi]_D$ −40, $[\phi]_{394}$ 0, $[\phi]_{350}$ +560 (pk), $[\phi]_{337}$ 0, $[\phi]_{302}$ −9820 (tr), $[\phi]_{291}$ 0, $[\phi]_{278}$ +9170 (pk), $[\phi]_{240}$ +7360!

2R-*Sakuranetin* (IId). ORD (*c*, 0·270, MeOH): $[\phi]_D$ +9·5, $[\phi]_{428}$ 0, $[\phi]_{350}$ −500 (tr), $[\phi]_{334}$ 0, $[\phi]_{300}$ +4880 (pk), $[\phi]_{289}$ 0, $[\phi]_{268}$ −6150 (tr), $[\phi]_{245}$ −2860!

2S-*Eriodictyol* (IIc). ORD (*c*, 0·335, MeCOMe): $[\phi]_D$ −47, $[\phi]_{415}$ 0, $[\phi]_{345}$ +1810 (pk), $[\phi]_{334}$ 0, $[\phi]_{303}$ −17,700 (tr), $[\phi]_{295}$ −13,300! ORD (*c*, 0·138, MeOH): $[\phi]_{450}$ −42, $[\phi]_{410}$ 0, $[\phi]_{350}$ +1250 (pk), $[\phi]_{337}$ 0, $[\phi]_{303}$ −14,600 (tr), $[\phi]_{291}$ 0, $[\phi]_{278}$ +14,600 (pk), $[\phi]_{250}$ +8360!

B. 3-*Hydroxyflavanones*

2R,3R-*Dihydroquercetin* (IIIa). ORD (*c*, 0·173, 50% MeCOMe–water): $[\phi]_D$ +127, $[\phi]_{350}$ +3170 (pk), $[\phi]_{336}$ 0, $[\phi]_{310}$ −21,100 (tr), $[\phi]_{296}$ 0, $[\phi]_{285}$ +30,800 (pk), $[\phi]_{250}$ +14,100!

2R,3R-*Dihydrorobinetin* (IIIb). ORD (*c*, 0·331, 50% MeCOMe–water): $[\phi]_D$ +75, $[\phi]_{343}$ +4000 (pk), $[\phi]_{336}$ 0, $[\phi]_{319}$ −31,800 (tr), $[\phi]_{304}$ 0, $[\phi]_{282}$ +34,000 (pk), $[\phi]_{245}$ +18,800 (pk), $[\phi]_{240}$ +9650! ORD (*c*, 0·955, MeOH): $[\phi]_D$ +7·0, $[\phi]_{343}$ +2870 (pk), $[\phi]_{337}$ 0, $[\phi]_{318}$ −31,000 (tr), $[\phi]_{280}$ +34,100 (pk), $[\phi]_{245}$ +29,300 (pk), $[\phi]_{230}$ +17,200!

2S,3S-*Dihydrofisetin* (IIIc). ORD (*c*, 0·883, 95% EtOH): $[\phi]_D$ −76, $[\phi]_{343}$ −2870 (tr), $[\phi]_{337}$ 0, $[\phi]_{319}$ +27,100 (pk), $[\phi]_{304}$ 0, $[\phi]_{282}$ −28,600 (tr), $[\phi]_{255}$ −8160!

C. *Flavanone and 3-hydroxyflavanone glycosides*

2S-*Liquiritin* (IIh). ORD (*c*, 0·156, MeOH): $[\phi]_D$ −295, $[\phi]_{340}$ +2010 (pk), $[\phi]_{335}$ 0, $[\phi]_{316}$ −24,100 (tr), $[\phi]_{298}$ 0, $[\phi]_{285}$ +5360 (pk), $[\phi]_{250}$ +12,100!

2R-*Sakuranin*. ORD (*c*, 0·295, MeOH): $[\phi]_D$ −470, $[\phi]_{323}$ −4110 (tr), $[\phi]_{313}$ 0, $[\phi]_{295}$ +7120 (pk), $[\phi]_{288}$ 0, $[\phi]_{260}$ −16,000!

2R,3R-*Astilbin*. ORD (*c*, 0·365, 50% MeCOMe–water): $[\phi]_D$ −14·8, $[\phi]_{355}$ +4010 (pk), $[\phi]_{338}$ 0, $[\phi]_{308}$ −32,700 (tr), $[\phi]_{295}$ 0, $[\phi]_{284}$ +24,700 (pk), $[\phi]_{250}$ +9250!

2R,2S-*Naringin* (IIf). ORD (*c*, 0·115, 95% EtOH): $[\phi]_D$ −441, $[\phi]_{347}$ −2430 (tr), $[\phi]_{315}$ −963 (pk), $[\phi]_{305}$ −1060!

2R-*Naringin* (IIf). ORD (*c*, 0·204, MeOH): $[\phi]_D$ −541, $[\phi]_{348}$ −4240 (tr), $[\phi]_{332}$ 0, $[\phi]_{314}$ +5410 (pk), $[\phi]_{299}$ + 5720 (pk), $[\phi]_{288}$ 0, $[\phi]_{265}$ − 11,000 (tr), $[\phi]_{250}$ − 9430! (This sample is approximately 27% optically pure.)

2S-*Hesperidin* (IIg). ORD (*c*, 0·012, MeOH): $[\phi]_D$ −605, $[\phi]_{365}$ −1750 (pk), $[\phi]_{298}$ −18,200 (tr), $[\phi]_{288}$ 0, $[\phi]_{272}$ +15,800 (pk), $[\phi]_{240}$ +5050!

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