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^{13}C NMR SPECTROSCOPY OF FLAVONOIDS+

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Abstract - A survey of ^{13}C NMR spectroscopy data of the various classes of flavonoids is presented which shows that the carbon resonances of ring C are useful in identification of the basic skeletal type. The applications of this data in structure elucidation studies such as determination of the positions of alkylation, acylation, glycosylation etc. are reviewed.

INTRODUCTION

The conventional methods of molecular structure determination of natural products by chemical degradative studies have undergone rapid changes in the last three decades with the introduction of new physical techniques such as NMR, Mass and X-ray etc. The sophistications introduced in these techniques in the last few years have been phenomenal which have vastly enhanced the capabilities of the chemists working on natural products. The ^{13}C NMR spectroscopy introduced around 1975 is the most recent addition and even in this short period a formidable and useful data has been generated on almost all classes of natural products. It was, therefore, considered worthwhile to compile and review the ^{13}C NMR spectroscopy data and its applications in the structure elucidation of flavonoids (Fig.1).

The characterisation of flavonoids was accomplished by absorption maxima in UV and visible regions and their shifts on addition of suitable reagents[1]. With the advent of ^{1}H NMR spectroscopy, applications of special techniques such as trimethylsilylation for solubilization of polyhydroxy flavonoids[2], solvent-induced shifts[3], lanthanide-induced shifts[4] and the

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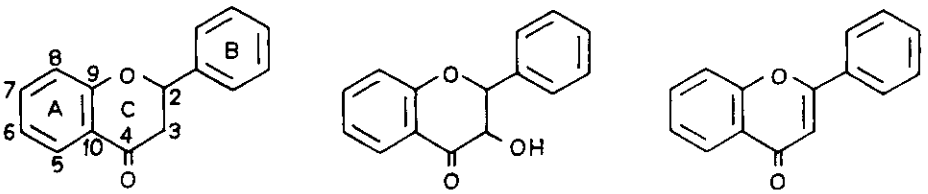
application of nuclear Overhauser effect (NOE) have been extensively and effectively used in structure determination studies.

The ^{13}C NMR spectrum with its wide chemical shift range of about 250 ppm (downfield from TMS) has proved of great help in structure elucidation of complex molecules[5]. Three types of spectra are generated in ^{13}C NMR spectroscopy: the proton-noise decoupled (PND) spectrum provides the information about the number and nature of carbon atoms depending on their respective chemical shifts; the single frequency off resonance decoupled spectrum (SFORD) gives the hydrogen substitution pattern where signals of carbons are split according to the number of attached hydrogen atoms; the proton-coupled spectrum gives $^{1}J_{CH}$, $^{2}J_{CH}$ and $^{3}J_{CH}$ coupling information in aromatic systems. These spectra are collectively used for the carbon resonance assignments of a molecule. Other assignment aids such as specific proton decoupling and deuteration studies have been rarely used so far.

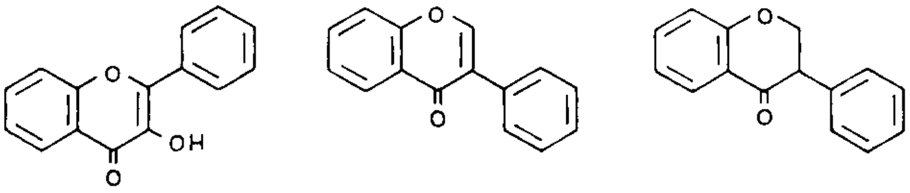
The first report of ^{13}C NMR of flavone appeared in 1974[6] and since then its application has been extended to all types of flavonoids such as flavones[7-19,35,88], isoflavones[7,13,17c,17d,20-26,35], flavonols[8,9,11,13,27-33], flavanones[7,8,17b,17c,33-42], isoflavanones[13,20,36,41c], flavanonols[8,13,20,28,36,42-45], flavans[46], isoflavans[13], flavan-3-ols[8,28], flavan-4-ols[46a], flavan-3,4-diols[28], flavonoid-O-glycosides[8,13,14,16,17c,27,35,47-60], acylated flavonoid-O-glycosides[14,55,61-66], flavonoid-C-glycosides[16,17,59,60,67-73], biflavonoids[34,74-78] and related compounds such as chalcones[7,8,11,79], dihydrochalcones and their glycosides[79a,79b], aurones[7,80], cyanidines[7,81-85] and **flavonolignans**[17,86-88].

The carbon resonances of flavonoids appear between 40 ppm to 200 ppm in ^{13}C NMR and may conveniently be divided into four regions: 40-85 ppm - C-2 and C-3 resonances of flavanones[33], isoflavanones[36], flavanonols[43] as well as methoxyl carbons; 90-110 ppm - C-6, C-8 and the two unsubstituted carbons of the trisubstituted ring B in flavones[7], isoflavones[11], flavanones[34], flavanonols[43], isoflavan[13] as well as C-3 of flavone[8]; 110 to 140 ppm - carbons of mono- or di-substituted ring B; 135 to 200 ppm - oxyaryl carbons, olefinic C-O (135-168 ppm) and carbonyl carbons (168-200 ppm). In alkyl substituted flavonoids the signals of carbons of alkyl chain generally appear below 40 ppm (Fig.2).

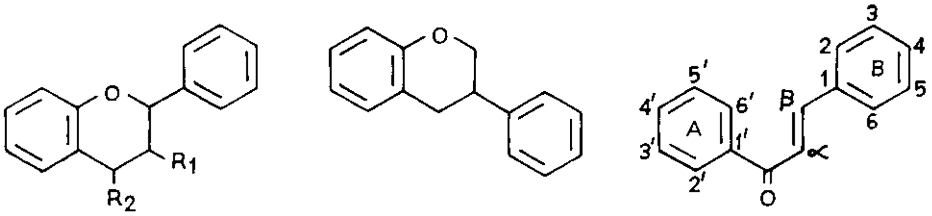
In this survey the ^{13}C NMR data of various skeletal types have been



I FLAVANONE II FLAVANONOL III FLAVONE



IV FLAVONOL V ISOFLAVONE VI ISOFLAVANONE



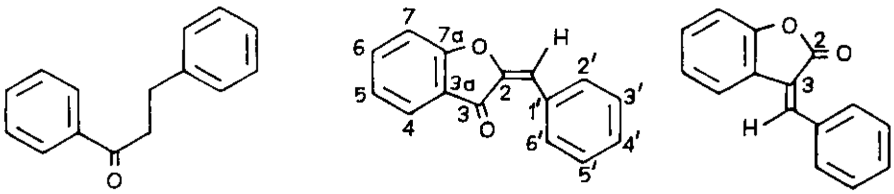
VII FLAVAN $R_1 = R_2 = H$

VIII $R_1 = OH$; $R_2 = H$

IX $R_1 = R_2 = OH$

X ISOFLAVAN

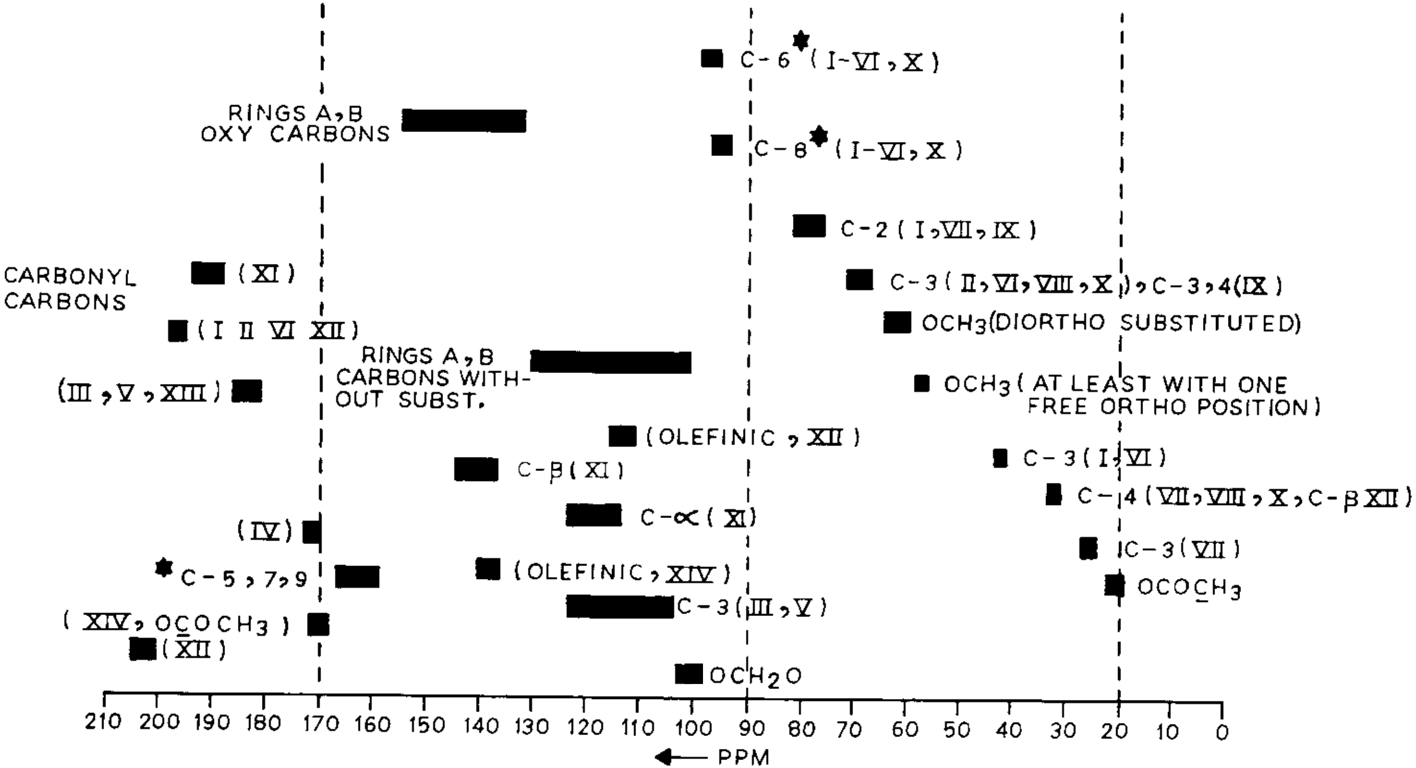
XI CHALCONE



XII DIHYDROCHALCONE XIII AURONE XIV ISOAURONE

FIG. 1

FIG. 2 CHARACTERISTIC SPECTRAL REGION IN CASE OF FLAVONOIDS AND RELATED COMPOUNDS



✱ IN CASE OF 5, 7 – DIHYDROXYLATED FLAVONOIDS consolidated in Tables 1-16. It is evident that the carbon resonances of ring C could be used in identifying the basic skeletal type (Table 17). The projection of this data as a valuable aid in structural elucidation studies such as determination of positions of alkylation, acylation and glycosylation etc. has been presented under the following sections:

1. 5,7-Dihydroxyflavonoids
1.1 Oxidation level of ring C
1.2 Ring A carbons and determination of site of alkylation
2. 5-Deoxyflavonoids
3. Flavans (including catechins, leucoanthocynidines)
4. Flavonoid glycosides
4.1 O-Glycosides
4.1.1 Site of glycosylation in flavonoid nucleus
4.1.2 Interglycosidic linkage in flavonoid-O-polyglycosides
4.2 Site of acylation in acylated flavonoid glycosides
4.3 C-Glycosides
4.4 Determination of ring size of the sugar and anomeric configuration
5. Biflavonoids
6. Chalcones and dihydrochalcones
7. Aurones and isoaurones
8. Determination of substitution pattern
8.1 Acetylation-induced shifts
8.2 Determination of site of methoxyl group and methylation-induced shifts
8.3 Trimethylsilylation-induced shifts

1. 5,7-Dihydroxyflavonoids

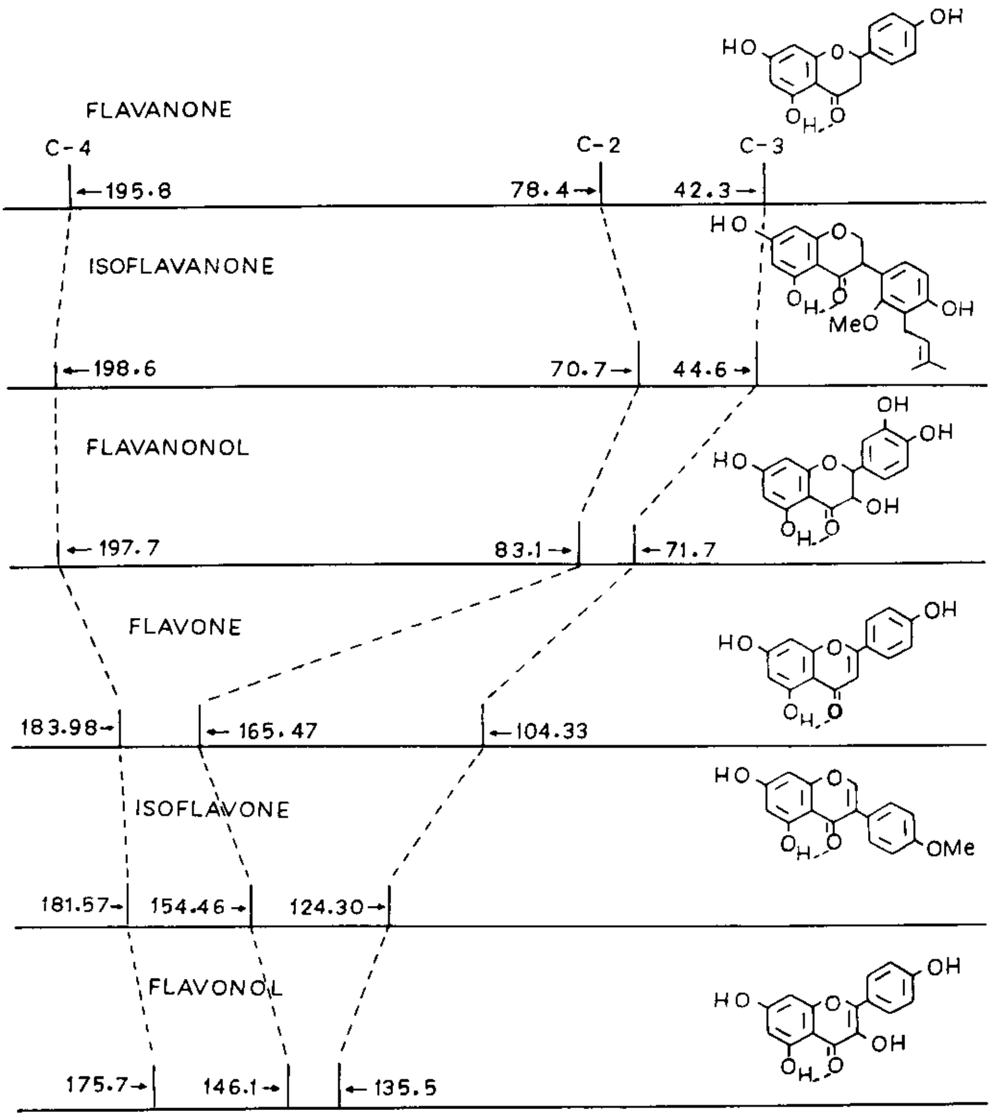
1.1 Oxidation level of Ring C - The δ values of carbons of rings A and C in 5,7-dihydroxylated flavonoids are given in Table 18. The chemical shift of carbonyl carbon directly reflects the oxidation level of central pyrone ring, which appears in 5,7-dihydroxyflavanone and flavanonol at 197 ± 1, in flavone and isoflavone at 181 ± 1[26] and in flavonols at 175-176 ppm. These values reflect the effect of the 2,3 double bond on the carbonyl polarization and being constant within a given series, serve as a diagnostic test for determining ring C oxidation level (Fig.2). The 5-OH group deshields the carbonyl resonance by ca. 5 ppm due to chelation effect and introduces coupling between phenolic H and ring A carbons ($J_{C_5OH_5} = \sim 5.0$; $J_{C_6OH_5} = \sim 4.5$; $J_{C_7OH_5} = \sim 1.5 Hz$)[89,90].

The proton-coupled spectra afford a clear distinction between the carbonyl carbon resonances of flavones and isoflavones. The latter appears as a doublet due to $^3J_{CH}$ interaction (ca. 7 Hz) with H-2[24]. On the other hand, C-2 signal in flavone appears as a sharp doublet due to absence of three bond interactions. This doublet has the largest C-H coupling (190-196.5 Hz) since C-2 experiences a considerable positive polarisation not only by the α-inductive effect of the oxygen but also due to a mesomeric electron withdrawing of the β-carbonyl group[17d,24]. In flavones the chemical shift of C-3 is usually 104 ± 1 but when methoxyl is attached to C-2' or C-6', a downfield shift to 112 ± 2 ppm is observed[10,18].

The chemical shifts of C-2 and C-3 are sufficiently characteristic and could be used to differentiate various categories of flavonoids (Fig.3). The saturation of C-2,3 double bond i.e. conversion of flavones to flavanones and flavonols to flavanonols, effects the chemical shifts as: (i) meta-oriented oxyaryl C-5,7,9 signals exhibit downfield shift in the rage of 1.5-6.0 ppm, (ii) the C-10 signal shows upfield shift and (iii) C-1' signal shows downfield shift of the order of 5-9 ppm due to loss of conjugation between rings B and C (Table 18).

1.2 Ring A carbons and determination of site of alkylation - Among the C-5, C-7 and C-9 carbons which usually appear between 157-167 ppm, the C-7 signal always appears at the lowest field in 5,7-oxygenated flavonoids[16-21]. For a large number of cases, C-6 and C-8 resonances appear between 90-100 ppm and are unambiguously differentiated by consideration of their multiplicities in the proton-coupled spectra, deuteration of 5-OH[89], specific proton decoupling[90] and shifts due to sequential methylation of 7-OH and 5-OH groups which showed that the C-6 signal is always at downfield position with respect to C-8 (Table 18). The chemical shift difference is small (ca. 0.9 ppm) in flavanones and larger (ca. 4.5 ppm) in flavones and flavonols. The assignments have also been made on the basis of relaxation time in case of 5,7,4'-trihydroxyflavanone[91].

FIG. 3 CORRELATION OF RING C CARBON RESONANCES IN 5,7-DIHYDROXY FLAVONOIDS



The position of alkyl substitution in ring A of flavonoids is deduced without any ambiguity by the downfield shift of the substituted aryl carbon signal by 6.0-9.6 ppm whereas the signal of the unsubstituted carbon (C-6 or C-8) is not essentially altered (± 0.5 ppm)[92,93]. The potentiality of this approach has been successfully utilized in structure establishment of C-methylated flavanone[8] and flavanonols[43], C-benzylated flavanones[37,38] and flavonoids possessing γ,γ-dimethyl alkyl group[36]. This information has been applied to revise the structures of chromeno and prenylated flavones isolated from Morus alba[19,94]. The coupling of substituted carbon with H of alkyl group in the proton-coupled spectra also provide useful information regarding the placement of alkyl substituent in 6 or 8 alkylated flavonoids[43].

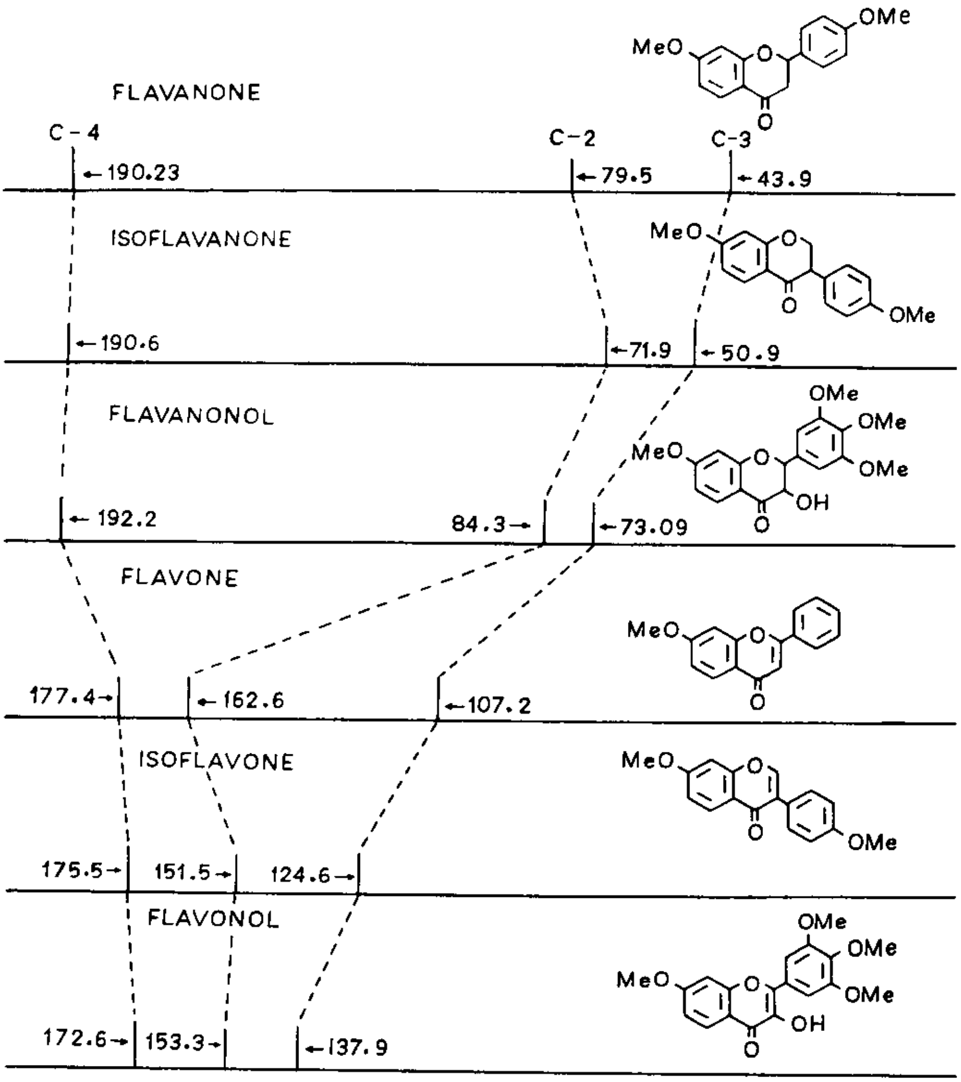
2. 5-Deoxyflavonoids

The deshielding effect on the carbonyl carbon resonance and the couplings of C-5,6,7 of ring A with H of 5-OH in 5,7-dihydroxyflavonoids, are altogether absent in 5-deoxyflavonoids. The respective C-5 carbon is observed at ca. 128-129.5 ppm in case of flavanones[8], isoflavanones[13] and flavanonols[28] and at ca. 126-127.5 ppm in case of flavones[28], isoflavones[7] and flavonols[28], hence suggesting the shielding (ca. 1-2 ppm) of C-5 due to C-2,3 double bond. As compared to C-5 hydroxylated products, the carbonyl C-4 signal now appears upfield ca. 5.0-7.5 ppm and has been observed in flavanones, isoflavanones and flavanonols at ca. 190-192.5 ppm, in flavones and isoflavones at ca. 175.0-177.5 ppm and in flavonols at ca. 172.5 ppm. These values clearly reflect the effect of 2,3 double bond on carbonyl polarization. The lack of intramolecular hydrogen bonding also causes deshielding (ca. 1-2 ppm) of C-2 and C-3 in flavanones and flavanonols, while in isoflavanone, C-2 exhibits the downfield shift of the same order but C-3 shows a little more deshielding (ca. 3.0-4.5 ppm). In isoflavone and flavonol the deshielding of C-2 and C-3 was remarkable where the shifts were of the order of 17.0 and 0.36 ppm, 7.0 and 2.5 ppm respectively[28] (Fig.4).

3. Flavans (including catechins and leucoanthocynidines)

There was so far only one report of ^{13}C NMR in the class of flavans (ring C unsubstituted) wherein C-2, C-3 and C-4 carbon resonances were observed at 78.7, 25.1 and 31.3 ppm respectively[46]. The isomeric isoflavan having aryl

FIG. 4 CORRELATION OF RING C CARBON RESONANCES IN 5-DEOXY FLAVONOIDS



substitution at C-3, exhibited deshielding (~ 7 ppm) of C-3 and shielding (~ 8 ppm) of C-2 while C-4 remained almost unaltered[13].

The introduction of OH function at C-3 as in flavan-3-ol, caused downfield shift of all the ring C carbon atoms. The ipso carbon (i.e. C-3) shifted downfield to an extent of 42.0-45.0 ppm (α effect) but the deshielding of C-2 (β effect) was almost double than that on C-4 which was deshielded by ~ 1.5 ppm[28]. By the introduction of another OH at C-4 i.e. in flavan-3,4-diol, C-2 was observed to be shielded by ca. 1.3 ppm whereas C-3 was deshielded by ca. 2.5 ppm and C-4 showed the expected deshielding due to OH substitution. A comparison of the chemical shifts for C-5, C-7 and C-9 in these compounds with flavonoids, indicated their higher field shifts (ca. 3.5-6.5 ppm) reflecting the marked effect of carbonyl on these carbons[28] (Fig.5).

4. Flavonoid glycosides

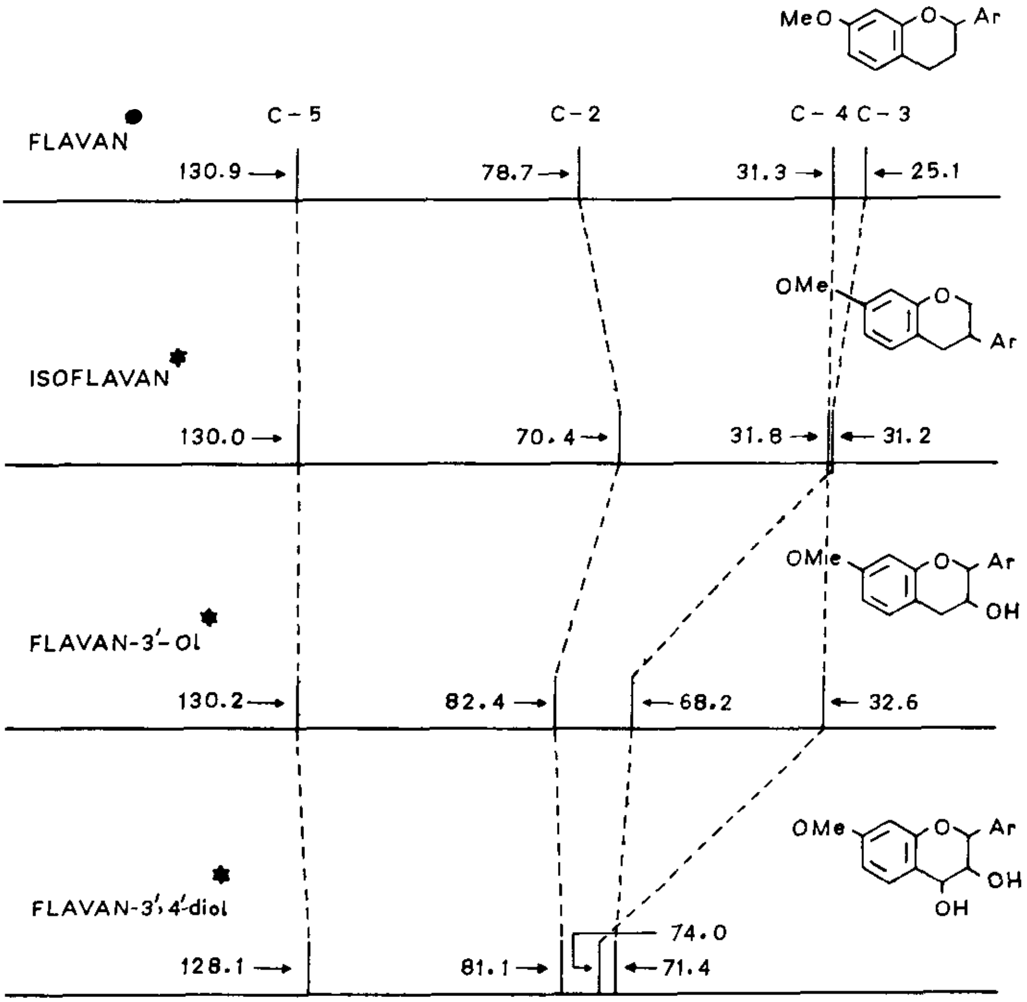
4.1 O-Glycosides

4.1.1 Site of glycosylation in flavonoid nucleus - Glycosylation of a phenolic hydroxyl induces upward shift in the resonance of the carbon directly involved in derivatisation[95]. When the 7-hydroxyl group is glucosylated the C-7 signal shifted upfield by 1.4-2.0 ppm whereas the signal of ortho carbons were shifted downfield (α effect) to a lesser extent (0.5-1.0 ppm) than the para C-10 signal which shifted downfield by 1.5-1.8 ppm[13]. Glycosylation with rhamnose appeared to have a more marked effect on the C-7 signal (-2.35 ppm) than with other sugars and this difference has a diagnostic value[14].

The same general pattern of signal shifts is also observed on glycosylation at C-3,3' and 4'. Glycosylation at C-3, however, produced a larger than anticipated effect on the C-2 signal (~ 9 ppm) in flavonols. This larger shift is more characteristic of olefinic than aromatic systems and it is likely here that this reflects the semiolefinic character of 2,3 double bond in flavonols. Glycosylation at either of the positions in 3',4'-dihydroxylated flavonoids produced upfield shift of the respective glycosylated carbon analogous to those mentioned above. However, the α-effect on hydroxyl-bearing ortho carbon was more marked and significant than the other ortho unsubstituted carbon[14].

Glycosylation of the 5-OH group has a profound effect on the electron density of the molecule due to absence of chelation. Thus, although the shift

FIG. 5 CORRELATION OF CARBON RESONANCES OF RING C AND C-5 IN 5-DEOXY-FLAVANS AND THEIR HYDROXY DERIVATIVES



● Ar (FLAVAN) = 3', 5' dihydroxy - 4' methoxy phenyl

✱ Ar (ISOFLAVAN, FLAVAN-3-ol, FLAVAN-3,4-diol) = 3', 4', 5'-trimethoxy phenyl observed in C-5 signal (-2.7 ppm) is similar to that expected for other sites, the downfield shifts for ortho and para (C-6,10,8) carbons were observed in the range of 3.0-4.5 ppm. A marked effect is also noticed in ring C carbon signals due to the loss of chelation, the C-2 and C-4 move upfield by about 3.0 and 6.0 ppm respectively whilst C-3 appeared ~ 2.5 ppm downfield in flavone glycosides[14]. Indeed, the shifts of ipso carbon together with those of ortho carbons provide a reliable guide to the site of glycosylation.

4.1.2 Interglycosidic linkage in flavonoid-O-polyglycosides - Glycosylation of a sugar hydroxyl produces a sizeable downfield shift on the resonance of this hydroxy-bearing carbon[96] which is of great value for elucidation of the interglycosidic linkages. Thus, it can be decided in a straight forward manner if the rhamnosyl unit is linked to glucose at C-6'' such as rutinosides [rhamnosyl (1'''→ 6'')glucosides] or at C-2'' such as neohesperidoside [rhamnosyl(1'''→ 2'')glucoside]. In rutinoside, the glucose C-6'' signal is shifted downfield by 4.5-6.0 ppm whereas in neohesperidoside the downfield shift of glucose C-2'' signal is 2.6-3.9 ppm[8,14]. When glucose is the glycosylating sugar as in sophorosides, however, a much larger downfield shifts of the order of 8 ppm is evident in the C-2'' signal[8,14]. The shift of such a magnitude appears to be typical of β-glucosylation in disaccharides and oligosaccharides. The glucosylation at C-2'' is also detectable by observing the adjacent C-1'' signal which is usually shifted upfield by ca. 2.9 ppm[77].

Assignments of sugar carbons can be made by the comparison with the reported data for monosaccharides[97] and methyl glycosides[98]. The spectra of di- and triglycosides were resolved by best-fit matching with the appropriate monosaccharide spectrum. *Hence, a comparison of the spectrum of a glycoside* with those of appropriate sugars in conjunction with glycosylation-induced shifts, could provide a considerable information on the establishment of structure of flavonoid polyglycosides.

4.2 Site of acylation in acylated flavonoid glycosides - The position of acyl substituent in acylated flavonoid glycosides could be assigned by comparative studies of their spectra with nonacylated equivalents, which clearly reveal the downfield shift of ca. 1.0-2.0 ppm for carbinyl carbon (C_α) while vicinal carbon (C_β) resonance is displaced upfield[99] (1.5-3.0 ppm) (acylation shift rule). Sometimes the deshielding of acylated glycosyl carbon was of much lower order but the shielding of adjacent carbons was good enough in determining acylation site. This rule has been successfully applied in the placement of acyl groups in acylated glycosides[61-66].

4.3 C-Glycosides - The most outstanding application of ^{13}C NMR has been in the structure elucidation of C-glycosides. The earlier chemical degradation methods like ferric chloride oxidation or ozonolysis[100] or mass spectral analysis of permethyl derivatives, are useful for characterisation of the C-linked sugars and to decide the position of linkage[101]. However, it was not feasible to determine the structure of sugar moieties by mass spectrometry.

Generally, C-glycosides possess sugar moieties either at C-6 or C-8 or at both positions in 5,7-dihydroxyflavonoids. Whatever may be the case, C-glycosylation causes a downfield shift (8-11 ppm) of the ipso signal which generally appears between 95-110 ppm[77]. In conformity with the earlier observation, the C-6 signal in this class as well appears downfield with respect to C-8 signal. In addition to the deshielding of ipso carbon, the ortho and para carbon signals are shifted upfield by 0.1-1.4 ppm[16]. Similar observations were also made in the case of xanthone C-glycoside, mangiferin[102].

4.4 Determination of ring size of the sugar and anomeric configuration - The coupling constant of the anomeric proton signal in ^{1}H NMR ($J_{H_{1''},H_{2''}}$) has limited utility in determination of anomeric configuration because the anomeric proton signal generally appeared as a broadened signal. The configuration has also been assigned by comparison of the molecular rotation differences $[(M)_D$ glycoside $- (M)_D$ aglycone$]$ with that of the corresponding methyl glycoside[103] or by the hydrolysis of glycosides with specific enzymes.

Methyl furanosides and methyl pyranosides of the same sugar have been found to be readily distinguishable by ^{13}C NMR and best-fit matching could give the information about the ring size[104,105]. Generally the signals of C-1" (anomeric carbon), C-2", C-3" and C-5" in β-D-glycosides appeared at remarkably lower field than those of the corresponding α-anomer. Recently, it has been reported that in pyranoses the coupling constant of C-1" signal ($^{1}J_{CH}$) was larger than those of the rest of carbons which usually varied between 143-148 Hz and did not depend much on stereochemistry. Further, $^1J_{C_{1''}H_{1''}}$ showed a clear dependence on orientation of the substituent at C-1'' e.g. in methyl glycosides $^1J_{CH}$ value of 158-162 Hz was observed when H-1'' was axial (β) whereas those with equatorial H-1'' (α) showed a higher value of 169-172 Hz[106,107]. Thus, $^1J_{CH}$ value is higher by 10 Hz in the case of α glycosides. Similarly, the sugar C-1'' signal of β-anomers appears at 100-102 ppm whereas the corresponding signal in α-anomers appears at ca. 95 ppm[108]. This data could be applied for the assignment of anomeric structure regardless of variety of the aglycone.

5. Biflavonoids

The majority of naturally occurring biflavonoids contain C-C linked monomers involving at least one ring A in inter-flavonoid linkage. The combinations so far found in the nature are (C-6, C-6''), (C-6, C-8''), (C-3', C-6''), (C-8, C-8''), (C-4', C-8'') and (C-3, C-8''). Biflavonoids having ether linkage fall in two groups - the hinokiflavone type (C-4'-O-C-6'') and ochanaflavone type (C-3'-O-C-4'')[71]. The solvent-induced shift of methoxyl signal on progressive addition of benzene-d_6[4] and the use of Eu(FOD)$_3$ reagent[109] in ^{1}H NMR spectroscopy had been applied so far for the determination of biflavonoid structures. ^{13}C NMR has now provided a reliable tool of wider applicability wherein the flavanyl substitution usually causes deshielding (4.5-9.9 ppm) of the signal of substituted carbons (as compared to monomeric model) but signals of the remaining carbons are not markedly effected and, therefore, this specific deshielding is valuable in identifying the inter-flavonoid linkage[74-78]. In specific cases of C-3,8'' linked biflavonoids, in addition to the normal deshielding of these carbons, C-2 signal is also deshielded to the extent of 3.0 ppm possibly due to steric factors[34]. In biluteolin octamethyl ether (a synthetic 5', 5''' linked biflavonoid), the C-5', 5''' resonances exhibited an unexpected downfield shift of 20.7 ppm which has also been stipulated as due to steric effects[78]. Thus, comparison of ^{13}C chemical shifts with monomeric equivalents along with consideration of inter-flavonoid-induced shifts could provide useful information in structure determination of biflavonoids.

6. Chalcones and dihydrochalcones

The ^{13}C NMR spectrum of cinnamic acid provides a good model for the assignments of chalcone carbons. The carbonyl carbon signal appears between 188.6-194.6 ppm and the resonances of α- and β-carbons are identified by their characteristic appearance as a six line multiplet in off-resonance decoupled spectrum at 116.6-128.1 and 136.2-145.4 ppm, each showing $J_{C\alpha/C\beta(H)}$=4.6 Hz[7,8]. It is of interest that the existence of 2-OH group in chalcone nucleus has pronounced shielding effect of 1.5-3.5 ppm on C_β and 0.4-1.0 ppm on C_α carbon[7,8]. Further, in 2'-hydroxy compounds the C-2' signal is shifted upfield by 14.9-15.6 ppm on acetylation[7].

In dihydrochalcones, the available data are limited to only one substance and its 2'-O-glucoside. The signals at ca. 44.5 and 30.0 ppm were assigned to C_α and C_β carbons and it was observed that glucosidation at C-2' position has pronounced effect on C=O and C_α carbons which were shifted upfield by ca. 5.5 and ca. 3.5 ppm, respectively[79].

7. Aurones and isoaurones

The ^{13}C NMR of isomeric five membered heterocyclic ring in aurones and isoaurones provides valuable information in distinguishing the isomeric equivalents[7]. In aurones, the olefinic and C-3 carbonyl resonances generally appear at 113 ± 2 and 183 ± 2 ppm whereas in isoaurones these are observed at 137-140 and 169 ± 2 ppm respectively. The C-3 resonance also exhibits marginal differences (1-2 ppm) in Z- and E-isomers enabling differentiation of the two series. However, the exocyclic olefinic carbon resonance was deshielded by ca. 9 ppm in E-isomer as compared to Z-isomer which provides additional data to differentiate the two series[81].

8. Determination of substitution pattern

The deviations from the predicted substituent-additivity parameters[110,111] are frequent specially in case of polysubstitution, but it is now possible to calculate the chemical shifts of aryl carbons of any type of substituted oxyflavonoid. The hydroxy and methoxy groups exert similar effect on the resonances of the aromatic carbons[112], but acetylation and methylation of a phenolic hydroxy group introduced characteristic spectral changes which usually enable the identification of the arrangement of these groups in flavonoid nucleus.

8.1 Acetylation-induced shifts - The methyl and carbonyl carbons of acetoxyl groups appear in a very narrow range i.e. 18-21 and 168-71 ppm respectively and recently an attempt has been made to determine acetoxylation pattern in acetylated isoflavones based on the position of carbonyl resonance but no generalisations have been recommended[26]. In flavonoid nucleus as in other phenolic substances[113-115], acetylation causes an upfield shift (6.5-15.6 ppm) of _ipso_ carbon whereas signals due to _ortho_ and _para_ carbons get deshielded by 4.0-12.2 ppm and 2-8 ppm respectively. The _meta_ carbon signals are slightly affected (0.9 to 4.3 ppm)[7].

The acetylation of ring C hydroxyl, however, did not follow the above generalisation and its effect differed significantly in magnitude as well as direction. In flavonols, 3-OH acetylation induces shielding of C-3, C-4 (3-5 ppm), C-1' (1-2 ppm) while the C-2 signal is deshielded by 0.8-2.5 ppm and C-10 signal is also shifted downfield (2-3 ppm). In flavanonols, the _ipso_ carbon signal did not show noticeable effect but C-2, C-4 signals were shifted upfield (2-3, 5-6 ppm respectively) and a downfield shift of C-10 by 1.2-1.5 ppm was observed[28]. In flavan-3-ol, 3-OH acetylation did not alter the C-3 resonance significantly (1.0-1.5 ppm) but introduced shielding of C-2 and C-4 to the extent of 3.2-4.5 ppm. The shielding of C-10 although not more than 1 ppm but was still significant. The acetylation of both OH in flavan-3,4-diol exhibited an upfield shift in the range of 1-5 ppm for C-2, C-3, C-4 and C-10 resonances[28].

8.2 Determination of site of methoxyl group and methylation-induced shifts - Majority of the carbon signals of methoxyl substituents in flavonoids appear in a very narrow range (55-57 ppm) but in some cases the signal gets relatively deshielded (4-8 ppm) when it is flanked by two bulky substituents such as hydroxyl[116], methoxyl[117], alkyl[118], O-aryl and C-aryl. This chemical shift variation was interpreted to be the result of a conformational change in the methoxyl group due to steric constraints. In unhindered aryl methoxyl, the nonbonding electrons of the oxygen atom are stipulated to be in conjugation with π electrons of the aromatic ring which requires the Ph-OCH_3 bond to be in the plane of ring. On di-ortho-substitution, steric crowding presumably perturbs this methoxy-aryl interaction i.e. reduced electron release from the aryl ring to oxygen atom, such that the polarisation of O-CH_3 bond is increased leading to conformation in which the methoxyl bond deviates from coplanarity with aryl ring[119,120] and hence deshielded. Similar observations were also made in methoxylated xanthones[117] and other compounds[121]. Recently, the abnormally high chemical shift of di-ortho-substituted methoxyl carbons have been related with longer relaxation time[122].

Methylation of a phenolic OH leads to an upfield shift (0.9-3.6 ppm) of the ortho carbon resonances (β-effect) while the ipso carbon is shifted (0.9-2.4 ppm) downfield (α-effect)with the exception of 5-OH where an unexpected upfield shift (0.2-2.0 ppm) of the ipso carbon signal and downfield shift of C-9 signal (1.7-1.9 ppm) (γ-effect) were observed. The carbonyl C-4 resonance also gets shifted by ca. 5 ppm upfield which is attributed to the redistribution of electron density on removal of hydrogen bonding on 5-OH methylation[93].

Methylation of 3-hydroxyl in flavonols, shifted C-3 and C-2 signals downfield to ca. 2.4 and 8.4 ppm respectively due to C-2,3 double bond and the C-4 signal was also shifted downfield by 2.0-2.5 ppm. Thus, although the shifts of the ipso carbons on methylation are found to be variable, the upfield shift of ortho carbon signal is very significant for providing information about the site of O-methylation. Further, in the proton-coupled spectra of methoxylated flavonoids, the signal for the ipso carbon is observed as broadened multiplet due to unresolved coupling (generally 3.5-4.2 Hz) with O-CH_3 hydrogens which is also useful in determining the position of methoxyl group.

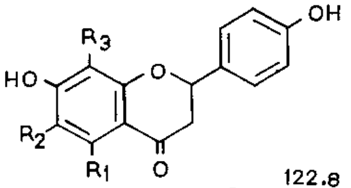
The methylenedioxy carbon appears at a very specific position (100-102 ppm) in a region where generally no other methylene would appear[30].

8.3 Trimethylsilylation-induced shifts - In flavonoids such as C-glycosides which are unstable in presence of air and decompose in DMSO-d_6, a convenient method of TMS ether formation is adopted. The trimethylsilylation shifts the ipso carbon to upfield and ortho and para carbons to downfield positions in 5,7-dihydroxyflavones. An upfield shift of 4-6 ppm and 2-5 ppm can also be observed for C-4 and C-2 signals respectively whereas C-3 resonance is shifted 2-4 ppm to downfield position[16].

Table 1 - ^{13}C Chemical Shifts for Flavanones (I)

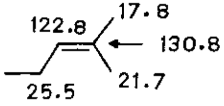
No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
1	-	72.4	44.6	191.6	126.9	121.4	135.9	117.9	161.3	120.8	138.6	125.9	128.6	128.6	128.6	125.9	7
2	7(OCH_3)	79.7	44.1	190.0	128.5	110.0	165.8	100.7	163.2	114.6	138.6	125.9	128.5	128.5	128.5	128.9	7
3	7,2'$(OCH_3)_2$	75.1	43.4	191.4	128.8	110.1	166.1	101.0	164.1	115.0	127.6	155.9	110.6	129.4	120.9	126.4	7
4	7(OCH_3),2'(OH)	74.9	42.6	190.3	128.1	109.7	165.6	100.8	163.6	114.5	125.3	154.2	115.5	129.0	119.0	126.5	7
5	7,3'$(OCH_3)_2$	79.6	44.1	189.9	128.4	109.9	165.8	100.8	163.1	114.6	140.2	111.7	159.7	113.7	129.6	118.1	7
6	7(OCH_3),3'(OH)	79.3	43.7	189.7	128.1	109.7	165.7	100.9	163.1	114.6	140.2	113.2	157.6	115.5	129.5	116.8	7
7	7,4'$(OH)_2$	79.5	43.9	190.2	128.4	109.8	165.8	100.7	163.2	114.6	130.6	127.5	113.9	159.6	113.9	127.5	7
8	7(OCH_3),4'(OH)	80.3	44.2	190.4	128.5	110.2	166.4	101.4	164.0	115.2	130.0	128.5	115.8	158.6	115.8	128.5	7
9	5,7$(OH)_2$	78.4	42.2	195.8	163.6	96.1	166.6	95.1	162.7	101.9	138.0	126.5	128.5	128.5	128.5	126.5	33
10	5,7,4'$(OH)_3$	78.4	42.0	196.2	163.6	95.9	166.7	95.0	162.9	101.8	138.0	128.2	115.2	157.8	115.2	128.2	33
11	5,7(OH_2), 4'(OCH_3)	77.8	41.9	196.1	163.5	95.8	166.6	94.9	162.7	101.7	128.9	128.6	113.5	159.4	113.5	128.6	33
12	5(OH),7,4' $(OCH_3)_2$	79.0	43.2	196.0	164.2	95.1	168.0	94.2	162.9	103.2	130.6	127.7	114.3	160.1	114.3	127.7	34
13	5,7,4'$(OCH_3)_3$	79.0	45.5	189.2	165.1	93.7	166.0	93.2	162.4	106.1	131.0	127.7	114.2	160.0	114.2	127.7	34
14	5,7,3',4'$(OH)_4$	78.3	42.2	196.2	163.4	95.7	166.6	94.8	162.8	101.7	130.5	114.2	145.1	145.6	115.3	117.8	33
15	5,7,4'$(OH)_3$, 3'(OCH_3)	78.7	42.1	196.3	163.5	95.7	166.6	95.0	162.9	101.8	129.4	111.1	147.5	146.9	115.2	119.6	33
16	5,7,3'$(OH)_3$, 4'(OCH_3)	78.5	42.1	196.2	163.8	96.2	166.9	95.4	163.0	102.1	131.4	114.3	146.7	148.1	112.1	118.0	33
17	5,7$(CH_3)_2$, 4'(OCH_3)	77.5	44.8	192.0	140.4	125.3	145.1	115.6	162.6	126.2	131.0	127.4	113.1	159.3	113.1	127.4	8

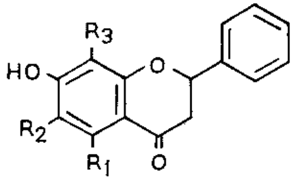
No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
18	5,7,8$(OCH_3)_3$	79.0	45.6	189.2	156.2	89.5	158.7	131.0	157.8	106.3	138.9	125.9	128.7	128.4	128.7	125.9	11
19		78.3	42.0	197.1	161.1	107.1	164.7	95.4	160.1		129.5	128.3	115.4	157.9	115.4	128.3	36
20		78.8	43.0	191.0	125.4	113.8	162.1	109.8	160.8	115.1	129.8	128.2	115.3	157.7	115.3	128.2	36
21		79.7	43.6	196.7	162.1	108.2	164.9	95.9	162.1	103.0	139.9	127.0	129.3	129.1	129.3	127.0	37
22		79.9	43.4	197.2	163.3	96.8	164.8	107.2	161.1	103.4	140.0	127.1	129.4	129.1	129.4	127.1	37
23		77.6	44.7	187.6	162.2	93.2	160.1	106.4	161.7	104.9	139.4						38
24		79.9	43.5	197.5	160.6	108.6	162.4	107.7	159.5	103.4	139.9	127.0	129.3	129.1	129.3	127.1	37
25		77.8	44.7	188.3	160.0	114.6	160.3	110.5	158.3	108.4	139.3						38
26		80.0	43.4	197.0	162.0	110.1	165.0	95.4	160.8	103.1	140.3	130.3	129.4	130.3	129.4	130.3	37
27		79.7	43.6	197.2	163.3	96.5	165.1	108.9	161.2	103.1	130.7	128.9	116.1	158.7	116.1	128.1	37
28		79.9	43.6	197.6	160.5	108.5	162.6	107.7	159.6	103.4							37
29		75.3	42.9	197.3	165.4	92.7	168.6	96.2	164.8	103.1	119.4	155.2	105.5	155.4	115.7	128.9	39
30		76.0	42.6	198.5	167.7	97.6	167.6	96.4	165.0	103.3	120.8	154.1	103.7	156.4	117.3	128.8	40
31	5,6,7,8$(OCH_3)_4$	79.4	45.9	189.6	152.5	138.7	153.4	141.1	150.2	111.6	137.9	128.8	125.9	128.6	125.9	128.8	41
32		78.0	42.3	196.3	155.6	108.1	158.8	102.2	159.4	101.8	129.8	127.1	115.0	155.8	115.0	127.1	42
33		78.3	43.1	195.6	156.1	108.1	158.8	102.5	159.3	102.3	138.4	125.6	128.4	128.4	128.4	125.6	42
34		79.5	43.4	196.5	161.7	108.6	164.7	95.0	161.3	102.5	130.9	114.2	145.4	145.8	115.7	118.6	41a
35		77.0	43.1	197.0	164.8	96.6	167.0	95.6	164.2	102.8	129.4	127.3	143.7	145.2	113.2	118.2	41a
36		76.9	43.3	197.0	161.8	108.7	164.4	95.0	161.8	102.7	129.5	127.1	143.6	145.1	113.2	118.1	41a



19: R_1=OH; R_3=H; R_2=

20: R_1, R_2=H ; R_3=





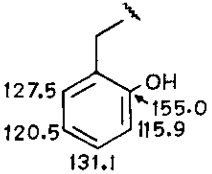
21 : R_1 = OH ; R_3=H ; R_2 =

22 : R_1 = OH ; R_2 = H ; R_3 =

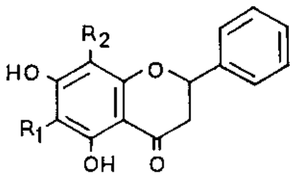
23 : R_1 = OCH_3 ; R_2=H ; R_3 =

24 : R_1 = OH ; R_2=R_3 =

25 : R_1 = OCH_3 ; R_2=R_3 =

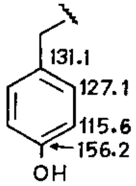


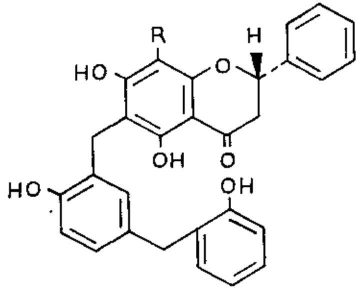
O-HYDROXY BENZYL



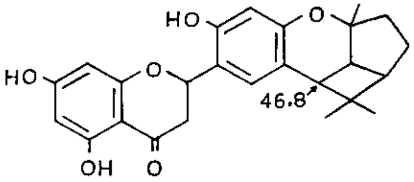
26 : R_2=H ; R_1 =

27 : R_1 = H ; R_2 =





28 : R = O-HYDROXY BENZYL



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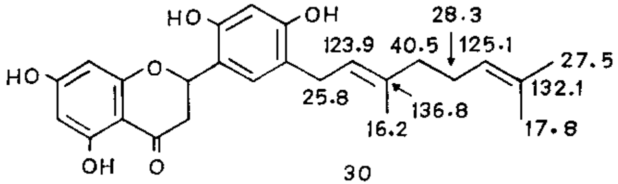
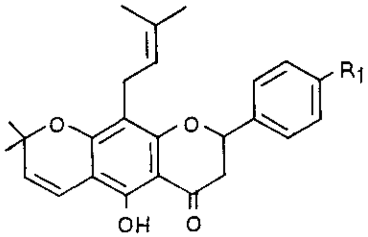
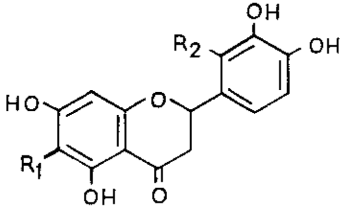


30



32 : R_1 = OH

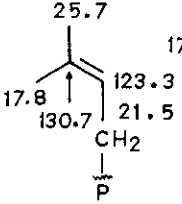
33 : R_1 = H



34 : R_1 = G ; R_2 = H

35 : R_1 = H ; R_2 = G

36 : R_1 = P ; R_2 = G



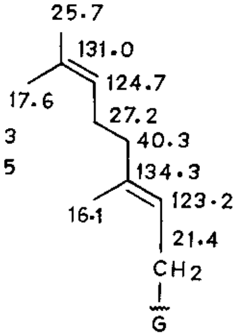
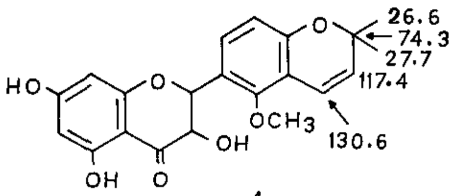


Table 2 ^{13}C Chemical Shifts for Dihydroflavonols (II)

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
1	5,7,3',4'$(OH)_4$	83.1	71.7	197.1	163.3	96.1	166.8	95.1	162.5	100.6	128.9	115.3	144.9	145.7	115.3	119.2	8
2	5,7,3',4'$(OCH_3)_4$	83.6	72.5	189.7	163.7	93.8	165.7	93.1	161.7	103.7	129.9	112.5	148.9	149.5	112.3	120.6	8
3	7,3',4',5' $(OCH_3)_4$	84.3	73.0	192.2	128.9	110.9	166.7	101.0	163.6	112.0	131.7	104.7	153.4	138.8	153.4	104.7	28
4		75.5	73.4	195.2	165.0	96.3	166.3	95.1	162.8	100.5	123.9	154.2	113.8	153.4	111.2	128.1	36
5	5,7,2',4'$(OH)_4$	78.3	70.9	198.4	163.7	96.5	169.6	95.5	163.3	100.9	114.2	159.0	103.0	157.5	107.1	130.3	13
6	5,7,2'$(OH)_3$, 4'(OCH_3)	82.7	71.5	197.3	163.2	96.0	166.8	94.9	162.3	100.3	129.6	147.8	119.1	115.0	146.1	111.6	45
7	5,7,3',4'$(OH)_4$, 6(CH_3)	84.3	73.1	197.7	165.2	104.8	161.7	95.1	161.3	101.0	129.6	115.6	145.4	146.2	115.5	120.6	43
8	5,7,3',4' $(OCH_3)_4$,6(CH_3)	83.4	72.9	190.8	162.5	106.0	165.2	95.6	159.0	104.5	129.1	110.6	149.3	149.3	111.3	120.4	43
9	5,7,3',4',5' $(OH)_5$,6(CH_3)	84.5	73.1	197.9	165.2	104.8	161.7	95.1	161.2	101.0	128.9	107.8	146.0	133.9	146.0	107.8	43
10		85.6	72.0	195.7	155.6	108.8	159.2	102.6	160.5	100.0	130.7	128.7	115.6	156.3	115.4	128.7	42
11		80.6	72.9	184.9	143.9	115.5	157.4	109.6	159.8	105.9	135.3	126.9	128.1	129.5	128.1	126.9	42



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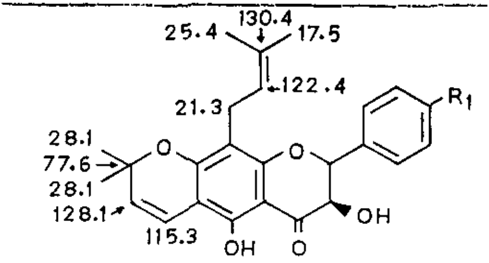


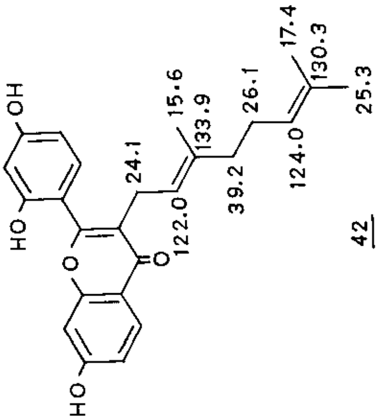
10: $R_1 = OH$ 11: $R_1 = H$

Table 3 ^{13}C Chemical Shifts for Flavones (III)

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
1	-	163.2	107.6	178.4	125.7	125.2	133.7	118.1	156.3	124.0	131.8	126.3	129.0	131.6	129.0	126.3	9
2	5(OH)	164.0	105.6	182.9	155.8	107.2	135.6	110.8	159.8	110.3	130.5	126.3	128.9	131.9	128.9	126.3	9
3	5(OCH_3)	160.6	108.7	177.8	159.4	109.8	133.4	106.2	157.9	114.0	131.9	125.6	128.6	131.0	128.6	125.6	10
4	6(OCH_3)		106.7		104.8		123.6	119.4				126.1	128.9	131.3	128.9	126.1	10
5	7(OH)	162.6	106.5	176.1	126.3	114.9	161.7	102.4	157.3	116.0	131.1	126.0	128.9	131.3	128.9	126.0	13
6	7(OCH_3)	162.6	107.2	177.4	126.7	114.1	163.7	100.2	157.7	117.6	131.6	125.8	128.7	131.1	128.7	125.8	10
7	8(OCH_3)	162.6	107.1	178.0	114.2	124.6	116.1	148.8	146.0	124.0	131.6	126.1	128.7	131.2	128.7	126.1	10
8	2'(OH)	160.8	111.1	177.3	125.2	124.8	134.1	118.5	155.9	123.2	117.8	156.7	117.1	132.6	119.5	128.6	18
9	2'(OCH_3)	160.6	112.5	178.7	125.4	124.6	133.3	117.8	156.2		132.8	157.8	111.6	132.2	120.5	129.1	10
10	3'(OCH_3)	162.8	107.5	178.0	125.4	124.9	133.2	117.9	155.9	123.7		111.5	159.7	116.9	129.8	118.5	10
11	4'(OH)	163.1	104.9	176.9	125.3	124.8	133.9	118.3	155.6	123.4	121.7	128.4	116.0	161.0	116.0	128.4	18
12	4'(OCH_3)	163.0	105.9	177.9	125.3	124.7	133.0	117.7	155.8	123.7	131.9	127.7	114.2	162.1	114.2	127.7	10
13	5,7$(OH)_2$	163.4	103.6	181.1	161.7	99.1	164.4	94.2	157.5	104.0	122.9	128.2	114.6	162.4	114.6	128.2	18
14	5(OH),7(OCH_3)	163.5	105.4	182.1	161.3	98.2	165.4	92.8	157.4	105.0	130.6	126.5	129.2	132.1	129.2	126.5	18
15	5,4'$(OH)_2$	165.4	103.9	183.4	156.4	108.0	136.1	111.4	160.1	110.4	121.9	129.1	116.7	161.6	116.7	129.1	9
16	5(OH),4'(OCH_3)	164.1	104.0	182.5	155.7	106.9	135.1	110.5	159.7	109.9	119.2	128.1	114.5	163.3	114.5	128.1	9
17	7,4'$(OH)_2$	162.7	104.7	176.6	126.6	115.0	162.7	102.7	157.6	116.3	122.0	128.3	116.1	160.9	116.1	128.3	18
18	7(OH),4'(OCH_3)	161.9	105.2	176.4	126.5	114.6	162.7	102.6	157.5	116.2	123.5	127.9	114.5	162.1	114.5	127.9	18
19	7,4'$(OCH_3)_2$	162.4	105.3	176.4	126.2	114.6	163.9	101.0	157.5	117.2	123.4	128.1	114.6	162.1	114.6	128.1	18
20	5(CH_3),7(OH), 4'(OCH_3)	160.0	106.1	178.1	141.2	116.5	160.9	100.7	158.5	114.2	123.0	127.5	114.2	161.5	114.2	125.5	13

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
21	5,7,4'$(OH)_3$	165.4	104.3	183.1	158.6	95.5	164.9	100.9	109.0	105.0	122.7	129.7	117.3	161.7	117.3	129.7	9
22	5,4'$(OH)_2$, 7(OCH_3)	163.9	103.9	182.3	157.9	99.4	164.8	94.3	162.2	104.4	123.5	128.4	114.8	162.8	114.8	128.4	35
23	5,7$(OH)_2$, 4'(OCH_3)	160.4	107.1	175.7	159.0	96.4	162.4	95.2	159.9	106.0	121.5	127.7	115.8	160.6	115.8	127.7	35
24	5(OCH_3),7, 4'$(OH)_2$	164.6	103.4	182.3	157.7	98.2	165.6	92.9	161.8	105.0	121.6	128.8	116.3	161.8	116.3	128.8	35
25	3',4'$(OH)_2$	164.1	105.3	177.9	125.1	125.0	134.4	118.4	156.1	123.5	122.8	113.1	145.8	149.5	116.2	119.4	9
26	3',4'$(OCH_3)_2$	162.6	105.7	176.6	125.0	124.6	133.6	118.1	155.6	123.7	123.3	110.5	149.3	152.2	112.4	119.9	9
27	5(OH),3',4', $(OCH_3)_2$	164.7	104.2	182.6	155.7	109.9	135.1	110.5	159.7	109.9	122.9	110.5	149.2	152.6	119.3	120.2	9
28	5,7,3',4'$(OH)_4$	164.5	103.3	182.2	157.9	99.2	164.7	94.2	162.1	104.2	119.3	113.8	146.2	150.1	116.4	122.1	35
29	5,7,4'$(OH)_3$, 3'(OCH_3)	163.7	103.8	181.8	157.4	98.8	164.2	94.0	161.6	103.3	120.4	110.2	150.8	148.0	115.8	121.7	35
30	5,7,3'$(OH)_3$, 4'(OCH_3)	163.6	104.0	181.8	157.5	99.0	164.4	94.0	161.7	103.7	118.7	113.1	146.9	151.2	112.1	123.3	35
31	5(OH),6,7 $(OCH_3)_2$	158.8	105.4	182.6	152.9	132.6	163.9	90.3	153.2	106.2	131.1	126.1	129.0	131.8	129.0	126.1	11
32	5,6,7$(OCH_3)_3$	157.7	108.3	177.0	152.5	140.4	162.0	96.3	154.5	112.2	131.5	125.9	128.9	131.2	128.9	125.9	11
33	3',4',5'$(OH)_3$	163.7	105.1	177.0	125.4	125.0	134.2	118.2	155.7	123.5	121.1	105.9	146.6	137.8	146.6	105.9	18
34	3',4',5' $(OCH_3)_3$	162.4	106.9	177.1	125.5	124.8	134.2	118.7	155.7	123.3	126.5	104.2	153.3	140.8	153.3	104.2	18
35	5,3',4',5'$(OH)_4$	163.1	104.8	176.6	126.8	115.1	162.8	102.5	157.6	116.3	121.4	105.7	146.5	137.5	146.5	105.7	18

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
36	5(OH),3',4',5'(OCH$_3$)$_3$	161.8	106.6	176.5	126.7	115.0	162.7	103.8	157.5	116.2	126.5	104.0	153.3	140.5	153.3	104.0	18
37	5,7,3',4',5'(OH)$_5$	164.2	103.2	181.6	161.6	99.0	164.2	93.9	157.5	104.0	120.9	106.0	146.5	137.9	146.5	106.0	14
38	5,7,4'(OH)$_3$, 3',5'(OCH$_3$)$_2$	164.0	103.6	181.6	157.2	98.7	163.5	94.1	161.3	120.8	139.7	104.3	148.0	164.0	148.0	104.3	15
39	5,7(OH)$_2$,3', 4',5'(OCH$_3$)$_3$	164.2	103.9	181.7	161.4	99.0	163.0	94.2	157.4	104.8	125.9	104.8	153.2	141.4	153.2	104.8	14
40	5,6,7,8,5'(OCH$_3$)$_5$,3',4'(OCH$_2$O)	160.6	100.3	177.1	151.5	138.3	147.6	138.0	148.3	114.8	125.9	107.2	144.1	149.6	143.8	106.7	17e
41	5,7,4'(OH)$_3$,6, 3',5'(OCH$_3$)$_3$	163.6	102.6	182.0	152.5	131.3	152.3	94.4	157.3	103.9	120.4	104.2	148.1	139.7	148.1	104.2	17e
42		160.3	121.2	176.2	126.6	114.4	162.1	101.9	157.7	115.5	111.9	160.0	102.9	156.1	106.5	130.8	13
43		159.0	119.4	181.7	161.1	105.5	161.6	98.0	155.0	103.6	111.3	160.3	102.8	156.5	106.7	130.9	13
44		158.5	120.1	181.7	161.1	100.5	161.7	98.9	151.8	104.4	110.9	160.6	130.6	156.6	107.1	131.1	13
45		152.8	104.4	177.7	153.6	107.0	155.7	104.6	152.2	108.3	108.9	114.8	137.5	150.3	105.6	140.8	88
46		163.2	105.5	181.8	155.3	104.7	158.7	94.8	156.3	104.7	130.4	126.2	128.8	131.8	128.8	126.2	94
47		158.5	120.9	183.3	151.2	98.9	162.9	106.9	162.9	105.1	113.2	161.0	104.4	162.4	108.0	132.3	19
48		158.2	121.8	183.6	156.8	98.5	162.6	107.9	162.0	104.1	113.1	153.9	104.1	160.3	108.1	132.1	19
49		159.5	121.5	183.1	152.9	99.6	162.7	105.6	162.7	101.3	112.7	158.5	104.5	162.7	108.1	132.3	19
50		159.7	117.7	181.7	152.2	99.9	163.6	104.5	161.3	101.4	114.2	151.1	112.3	162.4	109.0	130.7	19



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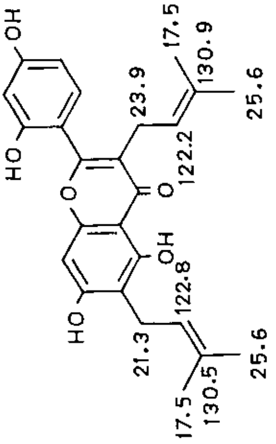

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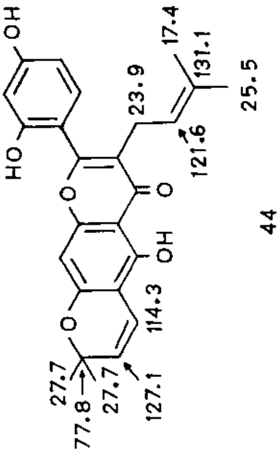

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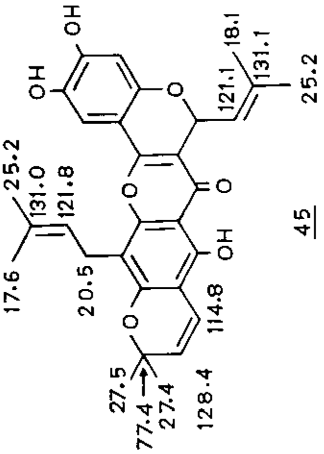

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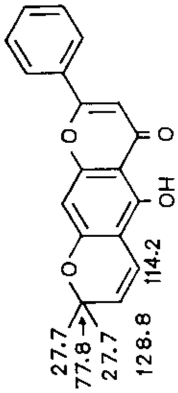

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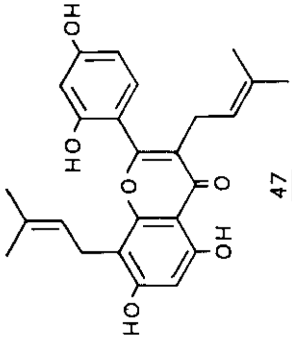

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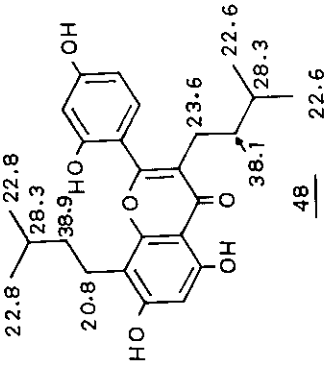

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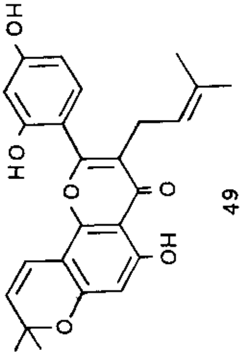

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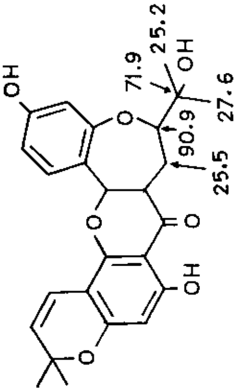

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Table 4 ^{13}C Chemical Shifts for Flavonols (IV)

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
1	3',4'$(OH)_2$	147.8	138.1	173.8	125.4	125.4	134.5	118.8	155.4	121.5	123.4	116.3	145.4	148.0	116.7	121.7	9
2	3',4'$(OCH_3)_2$	145.3	137.8	172.8	124.0	124.4	133.0	117.9	154.3	121.1	123.3	112.3	148.7	150.7	112.2	121.5	9
3	5,7$(OH)_2$	146.1	137.9	176.5	162.3	99.1	165.3	94.6	157.7		132.3	129.4	128.5	130.8	128.5	129.4	32
4	5,7,4'$(OH)_3$	146.1	135.5	175.7	156.0	98.2	163.8	93.4	160.5	102.9	121.6	129.3	115.3	159.0	115.3	129.3	27
5	5,7,2',4'$(OH)_4$	149.6	136.4	176.7	156.9	94.9	164.1	99.5	161.3	104.9	111.1	158.0	104.9	160.4	109.2	132.3	9
6	5,7,3',4'$(OH)_4$	146.9	135.8	175.9	156.2	98.3	164.0	93.5	160.8	103.1	122.1	115.2	145.1	147.7	115.7	120.1	33
7.	5(OCH_3),7,3',4'$(OH)_3$	142.0	137.1	171.1	158.1	96.0	162.6	94.8	160.6	105.2	122.4	114.6	145.1	147.1	115.7	119.3	33
8	5,3',4'$(OH)_3$,7(OCH_3)	147.3	136.0	175.9	156.0	97.4	164.9	91.8	160.4	103.7	121.9	115.2	145.0	147.8	115.6	120.1	33
9	5,3'$(OH)_2$,7,4'$(OCH_3)_2$	146.7	136.4	176.0	156.0	97.4	164.9	91.8	160.4	104.0	123.4	114.8	146.2	149.4	111.7	119.8	33
10	5,7,3',4'$(OCH_3)_4$	150.1	137.4	171.6	158.6	95.5	164.1	92.2	160.4	106.0	123.6	110.2	148.6	148.6	110.8	120.5	28
11	7,3',4',5'$(OCH_3)_4$	153.3	137.9	172.6	126.4	114.7	164.4	100.0	157.2	114.7	126.7	105.6	153.3	140.1	153.3	105.6	28
12	3,5,7$(OCH_3)_3$	152.0	141.4	173.6	160.5	95.5	163.5	92.1	158.4	109.1	130.5	127.7	128.0	129.0	128.1	128.7	13
13	3,6,7,3',4'$(OCH_3)_5$,5(OH)	151.4	138.0	180.0	151.9	131.5	158.0	89.8	155.0	105.7	122.1	110.7	148.0	150.8	110.3	121.5	13
14	3,5$(OCH_3)_2$,6,7(OCH_2O)	151.8	133.8	172.7		140.0	140.4	92.8	152.6	119.6	129.8	127.4	127.8	129.6	127.8	127.8	30
15	3(OCH_3),5,7$(OH)_2$	155.2	138.9	178.2	161.4	94.8	164.5	93.9	156.7	104.6	130.2	128.2	128.8	131.1	128.8	128.2	30a

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
16	3,4'(OCH$_3$)$_2$, 5,7(OH)$_2$	155.3	138.1	178.1	161.5	98.8	164.4	94.0	156.6	104.5	154.5	130.1	114.3	161.5	114.3	130.1	30a
17	3,3',4',5' (OCH$_3$)$_4$,5,7 (OH)$_2$	154.9	138.6	178.1	161.3	98.7	164.4	94.1	156.5	104.4	125.2	106.0	152.8	140.0	152.8	106.0	30a
18	5,7,3',4', 5'(OH)$_5$	147.1	136.1	176.0	161.0	98.5	164.2	93.5	156.4	103.3	121.2	107.5	146.0	136.1	146.0	136.1	30a

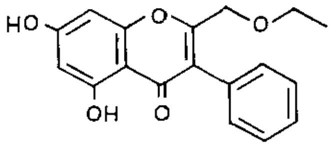
Table 5 ^{13}C Chemical Shifts for Isoflavones (V)

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
1	–	154.1	124.4	175.3	125.7	125.2	133.9	118.1	155.9	124.0	132.0	128.2	129.0	127.9	129.0	128.2	26
2	7(OCH$_3$)	152.3	125.1	175.3	127.6	114.4	163.8	100.0	157.7	118.3	127.9	128.2	128.8	131.7	128.8	128.2	7
3	7,2'(OCH$_3$)$_2$	153.8	122.6	175.4	127.8	114.3	163.9	100.2	158.0	118.6	121.1	157.6	111.3	131.8	120.6	129.7	7
4	7(OCH$_3$),2'(OH)	155.4	122.0	178.6	127.8	115.7	164.9	99.8	157.9	117.1	120.7	156.6	119.6	130.5	120.8	129.7	7
5	7,4'(OH)$_2$	152.2	122.6	178.5	127.1	115.0	162.6	102.1	157.6	116.8	123.9	129.9	115.0	147.3	115.0	129.9	26
6	7,4'(OCH$_3$)$_2$	151.8	124.6	175.5	127.5	114.3	163.7	99.9	157.7	118.2	124.0	129.6	113.7	159.3	113.7	129.9	7
7	7(OCH$_3$),4'(OH)	151.8	124.4	175.2	127.0	114.2	163.5	99.9	157.2	117.9	122.4	129.7	115.1	157.5	115.1	129.7	7
8	7(OH),4'(OCH$_3$)	152.2	124.4	175.1	127.2	115.1	162.7	102.3	157.7	117.0	123.8	130.0	113.6	159.2	113.6	130.0	7
9	5,7(OH)$_2$	155.1	124.1	181.3	163.9	100.2	165.1	94.6	159.0	106.2	132.1	129.9	129.0	128.9	129.0	129.0	20
10	6,7(OH)$_2$	152.8	123.1	174.7	108.4	144.8	152.4	102.8	151.2	116.9	132.6	128.9	128.0	127.5	128.0	128.9	26
11	6(OCH$_3$), 7(OH)	152.9	123.3	174.3	104.8	147.0	153.1	102.9	152.0	116.5	132.5	128.9	128.0	127.5	128.0	128.9	26

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
12	6(OH),7(OCH_3)	153.4	123.1	174.3	107.9	145.4	153.7	100.1	150.9	117.6	132.4	128.9	128.0	127.6	128.0	128.9	26
13	6,7$(OCH_3)_2$	153.2	123.6	174.3	104.3	147.5	154.3	100.0	151.9	117.2	132.3	128.9	128.1	127.6	128.1	128.9	26
14	7,8$(OCH_3)_2$	153.7	123.7	174.9	121.0	110.7	156.3	136.3	150.2	118.8	132.0	128.9	128.1	127.8	128.1	128.9	26
15	6,4'$(OCH_3)_2$	153.6	123.6	174.9	106.1	154.9	128.0	120.8	149.5	126.4	123.9	130.0	113.7	159.3	113.7	130.0	26
16	5,7,4'$(OH)_3$	153.6	121.4	180.2	157.6	98.6	164.3	93.7	157.6	104.6	122.4	130.0	115.2	162.1	115.2	130.0	35
17		151.2	123.9	181.5	162.8	99.6	161.1	94.0	157.5	105.1	122.8	131.5	113.5	160.2	113.5	131.5	17c
18	5,7$(OH)_2$, 4'(OCH_3)	154.4	124.3	181.5	163.9	99.9	165.0	94.5	159.0	106.2	123.8	131.0	114.5	161.7	114.5	131.0	20
19	5(OH),7,4' $(OCH_3)_2$	154.0	122.6	180.5	162.1	98.0	165.4	92.2	157.7	105.7	122.9	130.1	113.7	159.4	113.7	130.1	26
20	5,7,4'$(OCH_3)_3$	150.6	125.0	174.3	161.0	96.1	163.8	92.8	159.1	109.3	124.4	130.2	113.4	159.5	113.4	130.2	26
21	5,7$(OH)_2$,3',4' 5'$(OCH_3)_3$	154.3	122.5	180.0	162.3	99.2	164.5	93.8	157.7	104.7	126.4	106.6	152.8	137.7	152.8	106.6	26
22	6,7,4'$(OH)_3$	151.9	123.2	174.8	108.4	144.6	152.2	102.8	151.3	116.9	123.1	130.0	115.0	157.2	115.0	130.0	26
23	6,7$(OH)_2$, 4' (OCH_3)	152.3	122.7	174.6	108.3	144.6	152.2	102.7	151.1	116.8	124.7	130.0	113.5	158.9	113.5	130.0	26
24	6(OCH_3),7, 4'$(OH)_2$	152.0	123.4	174.7	104.8	146.9	152.9	102.9	152.0	116.5	122.9	130.0	115.1	157.3	115.1	130.0	26
25	6,4'$(OH)_2$, 7(OCH_3)	152.2	123.4	174.8	108.1	145.2	153.5	99.8	151.0	117.7	122.9	130.0	115.0	157.3	115.0	130.0	26
26	6,7$(OCH_3)_2$, 4'(OH)	152.2	123.6	174.6	104.3	147.4	154.2	100.0	151.9	117.2	122.7	129.9	115.0	157.3	115.0	129.9	26
27	6,4'$(OCH_3)_2$, 7(OH)	152.2	124.6	174.7	104.8	147.0	153.0	103.0	152.1	116.6	123.1	130.0	113.5	159.1	113.5	130.0	26

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
28	6(OH),7',4'$(OCH_3)_2$	152.5	122.9	174.6	108.0	145.3	153.6	99.9	151.0	117.6	124.6	130.0	113.5	159.0	113.5	130.0	26
29	6,7,4'$(OCH_3)_3$	152.4	123.4	174.7	104.4	147.5	154.3	99.9	152.0	117.3	124.4	130.0	113.6	159.2	113.6	130.0	26
30	7,8,4'$(OH)_3$	152.6	124.9	174.7	123.8	117.3	155.3	132.1	150.7	115.2	125.1	130.1	113.6	159.3	113.6	130.1	26
31	7,8$(OH)_2$,4'(OCH_3)	152.6	124.9	174.4	123.8	117.5	155.2	134.7	150.7	115.2	126.0	130.1	113.6	159.3	113.6	130.1	26
32	7,8,4'$(OCH_3)_3$	153.0	123.3	175.0	121.0	110.6	156.1	136.3	150.1	118.7	124.0	130.0	113.6	159.2	113.6	130.0	26
33	7,3',4'$(OCH_3)_3$	151.8	124.3	175.3	127.2	114.2	163.5	99.8	157.4	118.0	124.4	112.3	148.4	148.7	110.9	120.6	13
34	6,7,3',4'$(OCH_3)_4$	152.8	123.3	174.5	104.4	147.5	154.3	100.0	151.9	117.2	124.9	112.9	148.8	148.5	111.5	121.2	26
35	7(OCH_3),3',4'(OCH_2O)	151.8	124.7	175.2	127.6	114.2	164.0	99.7	157.4	118.1	125.5	109.4	147.4	147.4	108.0	122.2	20
36	5,7$(OH)_2$,2',4',5',6'$(OCH_3)_4$	154.5	119.3	180.6	152.5	130.9	156.3	93.6	153.0	105.5	110.4	151.6	97.8	149.6	142.4	115.0	13
37	5,6$(OCH_3)_2$,7(OH),3',4'(OCH_2O)	150.8	124.7	174.9	154.6	139.6	156.2	99.8	152.8	111.4	126.0	111.0	147.4	147.4	108.1	122.4	20
38	5,7,5'$(OCH_3)_3$,3',4'(OCH_2O)	150.4	125.6	175.3	156.3	93.0	156.9	130.4	152.0	109.7	125.7	110.0	147.5	147.5	108.1	122.5	20
39	5,6,7$(OCH_3)_3$,3',4'(OCH_2O)	150.7	125.6	175.0	154.6	140.7	157.8	96.1	153.1	113.6	125.7	110.0	147.6	147.6	108.3	122.6	20
40		151.9	125.1	175.4	126.4	114.8	157.2	109.0	152.2	118.4	131.8	128.1	128.7	127.8	128.7	128.1	23
41		151.6	124.6	175.7	126.6	114.8	157.0	109.2	152.5	118.3	124.2	130.1	113.8	159.7	113.8	130.1	23
42		151.8	124.4	175.5	126.4	114.8	157.2	109.0	152.3	118.2	124.4	112.5	148.8	149.1	111.1	120.8	23

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
43		151.6	124.9	175.4	126.6	114.7	157.0	109.0	152.8	118.2	125.6	109.6	147.5	147.5	108.2	122.2	23
44		152.1	122.6	180.6	159.2	99.9	162.0	100.7	151.8	105.7	123.2	129.7	113.7	159.5	113.7	129.7	23
45		151.7	124.2	175.3	123.4	119.6	157.8	103.7	157.2	118.4	124.2	130.0	113.8	159.3	113.8	130.0	23
46		152.3	122.9	180.7	156.8	106.1	159.6	94.7	157.1	105.2	123.3	129.9	114.0	159.6	114.0	129.9	23



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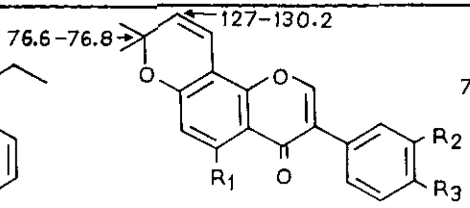
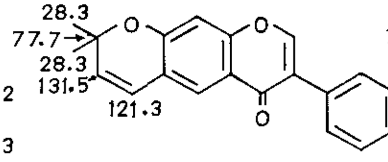


40: $R_1=R_2=R_3=H$ 41: $R_1=R_2=H$; $R_3=OCH_3$
42: $R_1=H$; $R_2=R_3=OCH_3$ 43: $R_1=H$; $R_2, R_3=OCH_2O$
44: $R_1=OH$; $R_2=H$; $R_3=OCH_3$



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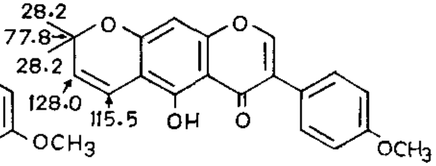

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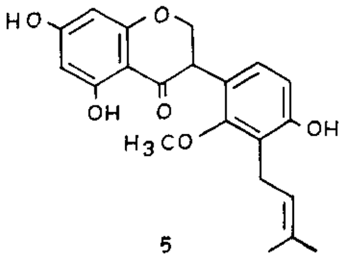
Table 6 ^{13}C Chemical Shifts for Isoflavanones (VI)

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
1	-	71.4	52.3	191.9	128.5	121.5	135.9	117.8	161.5	121.0	135.0	127.6	128.8	128.5	128.8	127.6	41b
2	7(OH),4'(OCH_3)	72.5	51.7	190.8	130.1	111.3	165.1	103.4	164.4	115.3	129.1	130.5	114.7	158.7	114.7	130.5	20
3	7,4'$(OCH_3)_2$	71.7	50.9	190.6	129.1	109.8	165.0	100.4	163.1	100.1	127.1	129.3	114.0	158.2	114.0	129.3	13
4	7,3',4'$(OCH_3)_3$	71.5	51.5	190.4	129.0	109.7	165.6	100.3	163.0	114.4	127.5	111.6	148.7	148.2	111.2	120.0	13
5		70.7	44.6	198.0	164.2	96.1	167.0	95.0	163.5	102.4	121.3	128.3	115.4	157.9	115.4	128.3	36
6		70.8	44.7	198.1	161.1	108.0	164.6	94.3	161.4	102.3	121.4	127.3	111.4	157.9	119.1	156.4	36



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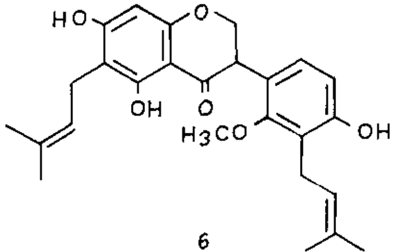

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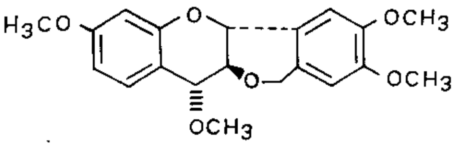
Table 7 ^{13}C Chemical Shifts for Flavans and Hydroxy flavans (VII,VIII, IX)

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
1	7,3',5'$(OH)_3$, 4'(OCH_3)	78.7	25.1	31.3	130.9	109.1	157.5	104.0	156.9	114.0	136.1	106.6	151.6	139.4	151.6	106.6	46
2	3,5,7,3', 4'$(OH)_5$	78.1	65.1	28.0	146.4	95.6	156.3	94.5	155.7	98.8	130.7	118.1	114.4	144.5	144.5	118.1	8
3	3(OH),5,7,3' 4'$(OCH_3)_4$	82.0	68.4	27.6	155.5	92.1	160.0	93.5	159.0	102.0	131.1	110.9	149.8	149.8	149.8	112.0	28
4	3(OH),7,3',4', 5'$(OCH_3)_4$	82.3	68.2	32.6	130.2	108.1	159.3	101.2	154.5	112.1	133.4	104.2	153.4	138.0	138.0	104.2	28
5	3,4$(OH)_2$,5,7, 3',4'$(OCH_3)_4$	80.7	73.7	70.3	155.7	92.8	160.9	93.7	159.3	105.8	129.3	110.3	149.3	139.3	111.2	120.5	28
6	3,4$(OH)_2$,7,3', 4',5'$(OCH_3)_4$	81.0	74.0	71.3	128.0	108.4	160.4	100.9	154.4	115.8	132.5	104.6	153.1	138.5	153.2	104.5	28
7		77.5	71.6	68.0	129.0	110.1	159.6	100.7	154.3	118.5	127.3	108.2	148.1	149.1	108.1	124.6	8
8	7,5'$(OH)_2$,3' (O-glu),4' (OCH_3)	78.6	24.9	30.9	130.9	109.1	156.8	104.0	157.5	114.3	137.7	109.1	151.7	139.4	152.0	106.0	46

No.	Substitution	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
9		76.9	40.1	65.9	128.7	121.0	128.2	116.8	154.5	126.1	140.5	127.0	129.2	125.8	129.2	127.0	46a
10		73.0	38.2	63.7	129.9	120.7	129.1	117.4	154.8	125.7	140.9	126.2	128.5	128.0	128.5	126.2	46a



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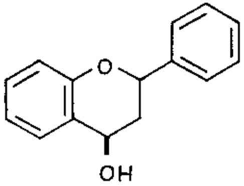

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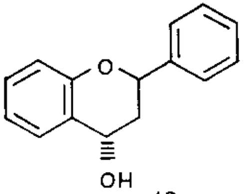

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Table 8 ^{13}C Chemical Shifts for Isoflavans (X)

No.	Substitution																
1	7,2',3',4' $(OCH_3)_4$	70.4	31.8	31.2	130.1	107.1	158.9	101.3	154.9	114.3	127.2	151.8	142.2	152.5	107.3	121.2	13
2	7,8,2',4' $(OCH_3)_4$,3'(OH)	70.3	31.4	31.5	123.9	106.3	147.2	134.6	146.8	115.1	127.0	145.1	138.5	146.4	106.9	116.7	13
3		69.6	32.5	30.1	130.1	108.1	154.9	103.0	154.5	114.1	122.0	145.8	137.1	142.2	132.4	116.3	13

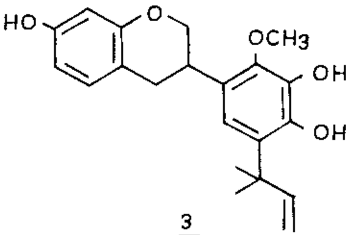

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Table 9 ^{13}C Chemical Shifts for Chalcones (XI) & Dihydrochalcones (XII)

No.	Substitution	β	α	CO	1'	2'	3'	4'	5'	6'	1	2	3	4	5	6	Ref
1	-	144.4	121.9	190.0	138.1	130.3	130.3	132.6	130.3	130.3	134.9	128.7	128.7	128.4	128.7	128.7	79
2	2'(OH)	145.2	118.4	193.5	119.3	163.5	118.7	136.2	119.9	129.6	138.4	128.9	128.5	130.8	128.5	128.9	7
3	$2,2'(OH)_2$	142.1	118.3	194.9	119.7	163.4	118.8	136.0	120.2	129.8	121.8	157.9	116.7	132.1	120.1	130.0	7
4	$2(OCH_3),2'(OH)$	141.1	118.5	194.3	120.2	163.6	118.7	136.1	120.8	129.7	123.7	159.1	111.3	132.2	120.8	129.6	7
5	$4(OCH_3),2'(OH)$	145.4	118.6	193.7	120.2	163.6	118.7	136.1	117.6	129.5	127.4	130.5	114.5	162.1	114.5	130.5	7
6	$2'(OH),4'(OCH_3)$	144.1	120.1	191.5	113.9	166.5	100.9	166.0	107.5	131.0	134.6	128.8	128.3	130.4	128.3	128.8	7
7	$2,2'(OH)_2,4'(OCH_3)$	141.1	119.7	192.8	114.3	166.5	101.1	166.0	107.3	131.5	132.0	157.7	116.7	131.8	120.4	129.9	7
8	$2,2',4'(OCH_3)_3$	137.5	127.8	191.1	124.6	160.4	98.7	164.0	105.2	132.8	122.6	158.7	111.2	131.2	120.7	128.7	7
9	$2,4,2'(OH)_3$	143.8	117.8	191.1	113.2	164.6	102.6	165.4	107.9	132.3	125.8	130.6	115.8	159.9	115.8	130.6	8
10	$4,4'(OCH_3)_2,2'(OH)$	143.9	117.4	191.4	113.9	160.3	100.9	165.7	107.2	130.9	127.2	130.1	114.2	161.5	114.2	130.1	7
11	$4(OH),2',4'(OCH_3)_2$	144.7	116.6	191.7	114.0	165.7	100.9	166.2	107.2	131.0	126.0	130.4	116.1	160.1	116.1	130.4	7
12	$4,2'(OH)_2,4'(OCH_3)$	144.8	116.7	191.7	114.1	166.3	101.3	165.9	167.3	131.2	126.1	130.6	116.2	160.3	116.2	130.6	7
13	$4,2',4'(OCH_3)_3$	142.3	125.3	190.2	122.6	161.6	98.8	164.4	105.5	132.9	128.4	130.2	114.6	160.6	114.6	130.2	7
14	$3,4'(OCH_3)_2,2'(OH)$	143.9	120.2	191.3	113.9	166.4	100.9	105.9	107.3	131.0	135.9	113.2	159.7	116.1	129.7	120.9	7
15	$3,2'(OH)_2,4'(OCH_3)$	144.4	119.8	191.6	113.9	166.3	100.9	165.9	107.2	131.3	135.8	135.0	157.6	118.1	129.7	120.0	7
16	$3(OH),4,2',4'(OCH_3)_3$	144.6	118.1	191.7	114.0	166.0	100.9	165.8	107.1	131.9	127.7	114.9	146.9	156.4	111.6	122.1	7

No.	Substitution	β	α	CO	1'	2'	3'	4'	5'	6'	1	2	3	4	5	6	Ref
17	2',4',5'(OCH$_3$)$_3$, 6'(OH)	142.6	127.4	193.2	106.8	158.6	130.8	159.4	87.1	158.5	135.4	128.9	128.3	130.1	128.3	128.9	11
18	2',4',5',6' (OCH$_3$)$_4$	144.6	128.8	193.2	116.6	153.3	136.2	155.0	92.7	151.8	134.8	128.8	128.4	130.3	128.4	128.8	11
19	4,6'(OH)$_2$,2', 4',5'(OCH$_3$)$_3$	143.4	123.8	192.5	106.9	157.1	130.2	157.4	88.3	156.0	125.6	130.5	115.9	160.3	130.5	115.9	11
20	4,4',6'(OCH$_3$)$_3$, 2'(OH)	142.4	125.3	192.6	106.5	162.6	93.9	168.5	91.3	166.1	128.5	130.1	114.4	161.5	114.4	130.1	34
21	4,2',4',6' (OCH$_3$)$_4$	143.8	127.1	193.8	112.2	158.8	91.0	162.4	91.0	158.8	127.7	130.0	114.4	161.5	114.4	130.0	34
22	4,2',4',6' (OCH$_3$)$_4$,3'(CH$_3$)	144.5	127.1	194.6	112.3	157.4	91.7	160.2	117.0	156.3	127.8	130.2	114.4	161.6	114.4	130.2	34
23	4(O-glu),2'(OH), 4',6'(OCH$_3$)$_2$	142.4	125.4	192.3	162.0	93.9	165.7	91.1	165.5	106.3	128.5	130.2	116.6	159.3	116.6	130.2	79c
24	4,2',4'(OH)$_3$	29.5	39.7	200.7	113.3	165.6	103.0	164.7	108.1	133.0							79a
25	4,2'(OH)$_2$,4' (OCH$_3$)	29.2	39.5	200.1	114.6	165.3	100.7	166.1	107.1	132.2	131.7	129.3	115.1	155.6	115.1	129.3	79a
26	4,4'(OH)$_2$,2' (O-glu)	30.2	44.7	204.7	121.2	158.7	104.0	162.6	111.0	133.3	133.8	140.4	116.1	154.4	116.1	130.4	79a
27	4(OH),2'(O-glu), 4'(OCH$_3$)	29.9	45.1	203.1	121.9	158.7	102.1	165.1	108.7	132.1	133.0	129.5	115.4	154.8	115.4	129.5	79a

Table 10 ^{13}C Chemical Shifts for Aurones (XIII)

No.	Substitution	2	3	4	5	6	7	7a	3a	=CH	1'	2'	3'	4'	5'	6'	Ref
1	-	146.8	184.5	124.5	123.3	136.7	112.8	166.0	131.5	112.8	132.2	131.4	128.8	129.8	128.8	131.4	80
2	5(CH_3)	148.5	182.8	124.1	132.4	138.0	112.1	163.8	123.3	122.2	131.9	130.8	128.4	130.2	128.4	130.8	80
3	6(OCH_3)	147.6	182.6	125.5	112.0	167.2	95.5	168.3	114.6	111.6	132.2	128.6	131.1	129.4	131.1	128.6	80
4	4'(OCH_3)	145.8	184.3	124.4	123.1	136.4	113.2	165.7	121.5	112.7	124.9	133.3	114.4	161.0	114.4	133.3	80
5	6(OCH_3),4'(OH)	146.0	182.4	125.2	112.7	166.9	96.4	167.8	148.8	111.9	123.4	133.2	116.1	159.3	116.4	133.2	7
6	4,6(CH_3)$_2$	147.4	184.8	134.5	126.1	148.2	110.1	166.8	117.4	111.9	132.6	131.2	128.7	129.3	128.7	131.2	80
7	4,6(CH_3)$_2$,4'(OCH_3)(Z)	146.4	184.7	139.4	125.9	147.8	110.1	166.6	117.7	111.6	125.3	133.0	134.3	160.7	114.3	133.0	80
8	4,6(CH_3)$_2$,4'(OCH_3)(E)	147.5	183.0	139.4	125.3	147.8	109.7	165.9	119.3	121.5	125.0	132.8	113.8	161.1	113.8	132.8	80
9	4,7(CH_3)$_2$(Z)	147.0	185.8	137.0	124.5	137.1	119.5	164.8	119.1	111.5	132.7	131.3	128.8	129.4	128.8	131.3	80
10	4,7(CH_3)$_2$(E)	148.1	184.0	137.0	123.8	137.1	119.5	164.2	120.6	121.3	132.0	130.7	128.3	129.9	128.3	130.7	80
11	4,7(CH_3)$_2$4'(OCH_3)(Z)	145.9	185.3	136.5	124.2	136.5	119.3	164.4	119.1	111.6	125.3	132.9	114.2	160.5	114.2	132.9	80
12	4,7(CH_3)$_2$,4'(OCH_3)(E)	147.0	183.5	136.5	123.5	136.5	119.1	163.7	120.7	121.7	125.0	132.8	113.6	161.1	113.6	132.8	80
13	4,6,7(CH_3)$_3$	146.4	183.3	136.0	126.5	147.6	117.7	165.0	117.0	110.7	132.8	131.1	128.7	129.1	128.7	131.1	80
14	6(OCH_3)	147.6	182.6	125.5	112.0	167.2	96.5	168.3	114.6	111.6	132.2	131.1	128.6	129.4	128.6	131.1	80
15	5(OH),6(OCH_3)	146.0	182.4	125.2	112.7	166.9	96.4	167.8	114.8	111.9	123.4	133.2	116.1	159.3	116.1	133.2	80
16	6(OCH_3),2'(OH)	146.8	181.7	124.9	111.9	166.8	96.5	167.7	114.4	105.9	119.0	157.5	115.6	131.1	119.3	130.9	80
17		143.1	102.4	124.2	110.9	165.7	95.0	165.9	115.6	127.8	128.4	130.2	114.6	157.1	114.6	130.2	80

Table 11 ^{13}C Chemical Shifts for Isoaurones (XIV)

No.	Substitution	2	3	4	5	6	7	7a	3a	=CH	1'	2'	3'	4'	5'	6'	Ref
1	-	168.6	122.1	123.4	122.6	130.3	111.0	154.2	128.3	140.6	133.8	128.6	129.1	130.7	129.1	128.6	7
2	6(OCH_3)	169.8	122.3	124.0	110.1	162.6	97.5	156.4	114.8	137.8	134.8	129.8	129.5	130.4	129.5	129.1	7

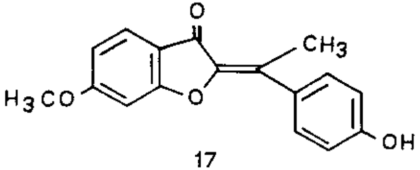

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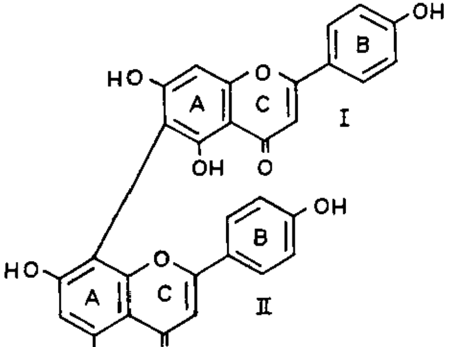
Table 12 ^{13}C Chemical Shifts for Biflavonoids

No.	Moiety	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
	I-A & II-A ring linked biflavonoids																
Flavone-Flavone linked																	
1	I	164.1	103.1	182.3	160.0	103.6	162.9	93.7	157.0	103.8	121.5	128.6	116.2	161.3	116.2	128.6	74
	II	163.9	102.8	182.1	160.9	98.9	162.7	99.4	155.1	104.0	121.7	128.2	116.2	161.2	116.2	128.2	
2	I	163.9	102.8	182.1	161.3	99.0	162.7	98.7	155.3	104.3	121.7	127.9	116.1	161.1	116.1	127.9	74
	II	163.9	102.8	182.1	161.3	99.0	162.7	98.7	155.3	104.3	121.7	127.9	116.1	161.1	116.1	127.9	
3	I	161.0	106.0	177.7	161.6	91.6	164.8	102.0	160.4	107.7	123.4	107.7	148.8	151.4	111.0	118.9	77
	II	161.0	106.0	177.7	161.6	91.6	164.8	102.0	160.4	107.7	123.4	107.7	148.8	151.4	111.0	118.9	

No.	Moiety	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
Flavanone-Flavone linked																	
4	I	78.7	42.2	196.5	161.8	100.3	165.2	94.8	162.4	101.9	129.1	128.2	115.5	157.9	115.5	128.2	74
	II	163.8	102.8	182.3	160.7	98.8	162.8	99.5	151.9	103.9	121.7	128.4	116.2	161.2	116.2	128.4	
Flavanone-Flavanone linked																	
5	I	78.5	42.2	196.3	161.8	101.1	165.3	94.7	161.9	101.9	129.3	128.3	115.4	157.8	115.4	128.3	74
	II	78.5	42.2	196.3	161.9	101.1	165.3	94.7	161.9	101.9	129.3	128.3	115.4	157.8	115.4	128.3	
6	I	78.6	42.3	196.4	161.8	101.2	165.2	94.6	162.7	107.8	129.2	128.1	115.4	157.7	115.4	128.1	74
	II	77.9	42.1	196.3	161.8	95.7	165.2	100.3	161.6	102.1	129.2	127.6	115.3	157.3	115.3	128.1	
	I-A & II-B ring linked biflavonoids																
Flavone-Flavone linked																	
7	I	164.1	102.9	181.7	161.5	99.0	163.7	94.0	157.5	103.9	121.4	127.2	120.8	159.7	116.7	131.0	74
	II	164.1	102.9	181.8	160.0	103.5	163.1	93.9	156.6	103.9	121.6	128.3	116.1	161.1	116.1	128.3	
	I-B & II-A ring linked biflavonoids																
Flavone-Flavone linked																	
8	I	164.0	103.2	181.8	160.6	98.9	163.9	94.2	157.6	104.0	121.3	127.9	121.6	159.6	116.4	131.6	74
	II	164.3	102.8	182.2	160.8	99.1	162.0	104.1	154.7	104.0	120.3	128.3	116.0	161.6	116.6	128.3	
Flavanone-Flavanone linked																	
9	I	78.7	42.3	196.7	163.6	95.8	166.7	95.1	157.1	102.1	131.2	128.3	115.1	160.2	120.1	126.9	76
	II	77.9	41.6	196.2	162.5	95.7	164.7	105.9	155.9	101.1	129.1	127.8	115.1	163.1	115.1	127.8	
	I-C & II-A ring linked biflavonoids																
Flavone-Flavone linked																	
10	I	164.4	103.3	182.3	162.1	99.3	164.4	94.3	157.7	104.2	121.4	112.7	145.9	148.6	120.6	122.7	77
	II	164.4	103.3	181.9	161.0	99.3	161.8	104.2	155.0	104.2	122.4	114.1	146.2	149.8	116.1	119.1	

No.	Moiety	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
Flavanone-Flavone linked																	
11	I	81.4	48.2	196.0	163.7	96.4	166.6	95.3	163.7	101.7	128.1	128.1	114.6	162.0	114.6	128.1	74
	II	163.7	102.8	181.6	160.4	98.5	162.8	100.6	157.3	103.7	121.3	128.1	115.9	161.0	115.9	128.1	
12	I	81.0	48.7	195.6	163.5	96.2	166.3	95.2	162.5	101.5	128.0	128.1	114.4	157.1	114.4	128.1	34
	II	163.2	102.8	181.4	160.3	98.6	161.4	100.2	155.0	103.2	131.1	131.1	145.4	149.4	116.1	119.0	
Flavanone-Flavanone linked																	
13	I	81.4	47.7	195.2	163.4	96.0	165.9	95.0	162.3	101.3	127.9	128.5	114.5	157.1	114.5	128.5	34
	II	78.3	43.0	196.1	162.3	94.9	164.3	101.3	162.0	101.0	128.9	127.3	114.9	157.1	114.9	127.3	
14	I	82.1	48.8	197.2	164.4	95.3	167.7	94.1	163.0	103.2	130.2	128.6	113.5	159.9	113.5	128.6	34
	II	79.1	46.1	189.5	164.4	89.2	167.7	102.9	162.0	106.0	130.9	127.8	114.1	159.9	114.1	127.8	
Flavanone-Flavanonol linked																	
15	I	82.7	47.3	197.4	163.7	96.1	164.6	95.0	162.7	101.3	129.8	127.7	114.8	157.7	114.8	126.7	76
	II	82.7	70.0	196.5	163.7	96.1	164.6	101.1	162.1	101.1	128.8	111.8	146.2	146.2	114.8	128.8	
16	I	79.6	45.2	195.4		94.0		93.0		99.2	126.1	126.9	112.8	155.7	112.8	128.9	76
	II	80.8	70.0	194.5		93.0				99.2	125.9	112.8	142.8	143.6	112.8	126.9	
17	I	82.6	48.9	197.7	161.5	95.6	165.2	95.6	164.9	102.4	129.4	115.4	145.0	145.1	115.4	120.2	78
	II	84.0	73.1	197.7	161.5	96.8	166.7	102.6	163.9	102.4	129.4	115.7	145.0	149.7	115.7	120.2	
Flavanone-Chalcone linked																	
18	I	81.7	51.0	193.7	164.9	93.1	162.1	105.8	130.3	128.2	113.2	159.1	113.2	159.1	113.2	128.2	34
	II	144.4	126.4	189.3	157.5	91.5	159.0	115.4	157.1	110.5	127.2	129.2	113.9	161.0	113.9	129.7	
19	I	81.6	51.1	193.4	164.5	93.4	165.0	93.0	162.0	105.7	130.3	128.1	113.1	159.1	113.1	128.1	34
	II	144.6	126.6	180.2	157.3	91.6	159.1	115.4	157.1	110.5	127.3	109.9	148.8	150.9	110.9	122.8	

No.	Moiety	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
	I-C & II-C ring linked biflavonoids																
Flavone-Flavone linked																	
20	I	160.6	108.5	177.3	160.0	92.7	163.8	96.2	159.6	109.0	126.5	109.3	149.5	152.9	132.2	120.9	77
	II	160.6	108.5	177.3	160.0	92.7	163.8	96.2	159.6	109.0	126.5	109.3	149.5	152.9	132.2	120.9	



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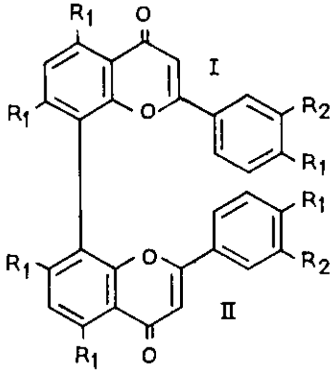
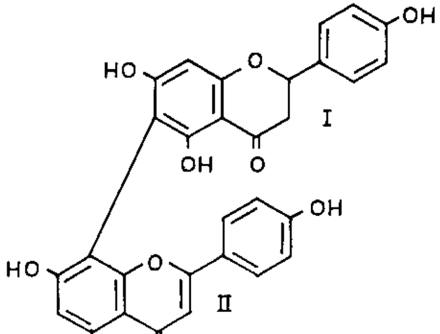


2: $R_1 = OH$; $R_2 = H$

3: $R_1 = R_2 = OCH_3$



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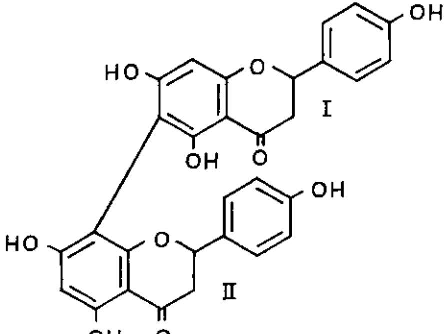

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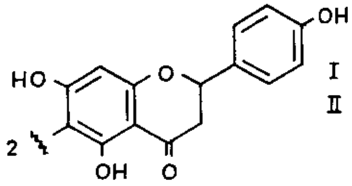

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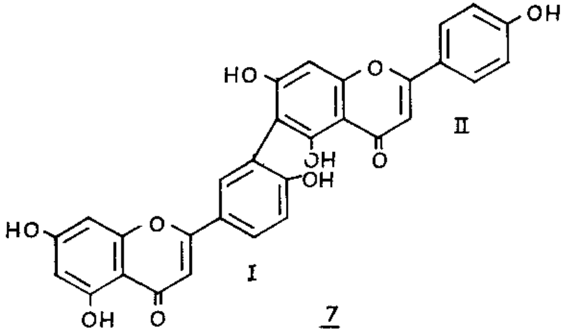

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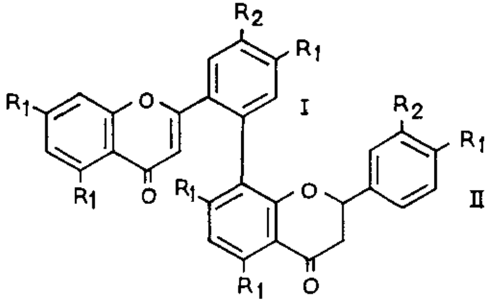
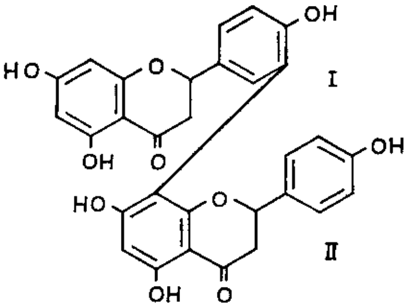


8: $R_1 = OH$; $R_2 = H$
10: $R_1 = R_2 = OH$



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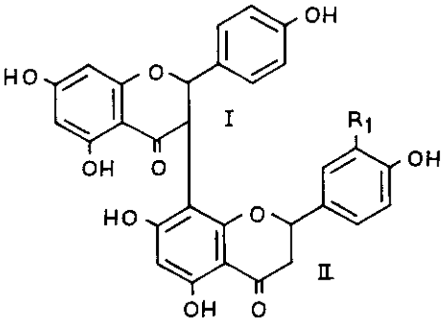
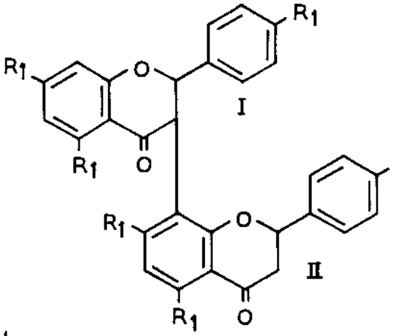
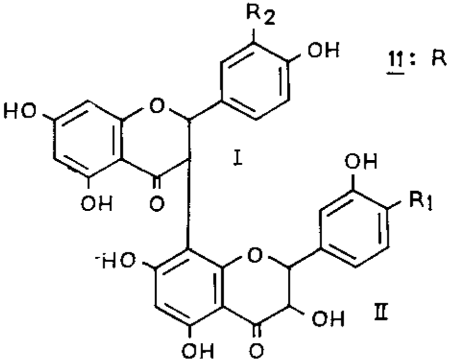


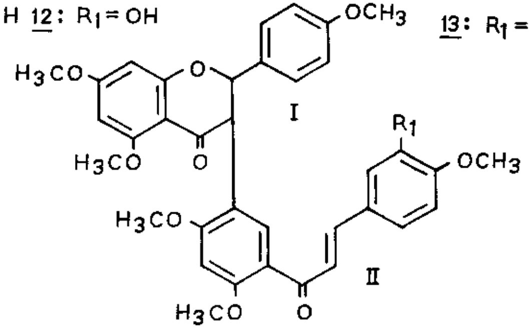
11: $R_1 = H$ 12: $R_1 = OH$



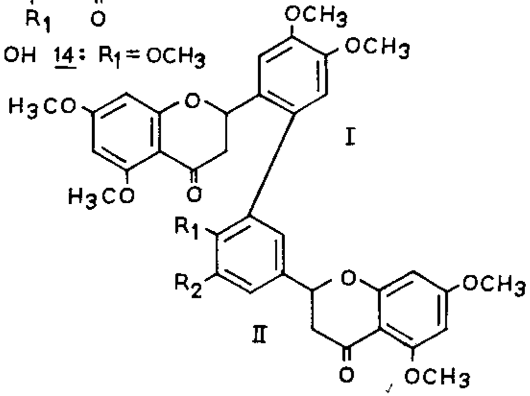
13: $R_1 = OH$ 14: $R_1 = OCH_3$



15: $R_1 = OCH_3$; $R_2 = H$
16: $R_1 = OH$; $R_2 = H$
17: $R_1 = R_2 = OH$



18: $R_1 = H$ 19: $R_1 = OCH_3$



20: $R_1 = R_2 = OCH_3$

Table 13 ^{13}C Chemical Shifts for Flavonoid-O-glycosides*

No.	Name**	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
	Flavone-O-glycosides																
Flavone-O-monoglycosides																	
1	Ap-7-glu	163.3	103.3	182.3	157.2	99.7	164.6	95.1	161.9	105.6	121.1	128.8	116.3	161.3	116.3	128.8	35
2	Lu-5-glu	162.3	105.7	176.6	158.3	104.3	161.3	98.1	158.4	108.5	121.8	113.2	145.6	149.0	116.0	118.3	14
3	Lu-7-glu	164.5	103.2	181.6	161.1	99.7	162.9	94.9	156.9	105.5	121.6	113.7	145.7	149.7	116.0	119.0	14
4	Lu-3-glu	164.1	103.4	181.7	161.4	99.0	163.5	94.1	157.4	103.9	121.2	115.3	145.6	150.9	116.6	121.6	14
Flavone-O-diglycosides																	
a. with sugars linked to one oxycarbon																	
5	Ap-7-glu-(2→1)-ap	164.2	103.3	181.9	161.3	98.8	162.8	95.0	157.0	105.6	121.3	128.5	116.1	161.2	116.1	128.5	14
6	Ac-7-rut	163.2	104.3	182.4	157.4	100.8	164.4	95.1	161.6	105.8	123.1	128.1	115.0	162.9	115.0	128.8	55
7	Pseubap^{+}	153.7	123.4	174.5	126.9	115.6	161.4	103.9	156.9	118.2	125.6	109.3	147.0	147.0	107.9	122.2	8
b. with sugars linked to different oxycarbons																	
8.	Lu-7,3'-glu	164.2	103.3	181.9	161.3	98.8	162.8	95.0	157.0	105.6	121.3	128.5	116.1	161.2	116.1	128.5	
Flavone-O-triglycoside																	
9	Ap-7-glu-(2",4")-rha	164.4	103.1	181.9	162.0	99.1	162.4	94.8	157.0	105.5	120.6	128.6	116.3	161.2	116.3	128.6	48
10	Di-7-glu-(2",4")-rha	164.1	103.9	181.9	161.1	99.3	162.4	94.3	157.0	105.5	122.8	112.1	146.8	151.3	113.1	118.9	48
	Flavonol-O-glycosides																
Flavonol-O-monoglycosides																	
11	Ka-7-glu	147.9	136.0	176.1	160.5	99.2	162.9	94.8	156.0	105.0	121.7	129.6	115.6	159.4	115.6	129.6	14
12	Qu-7-glu	147.9	135.9	175.9	160.3	98.9	162.7	94.5	155.7	104.7	121.9	115.5	145.0	147.8	115.4	120.1	14

No.	Name**	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
13	Qu-4'-glu	147.0	136.5	176.3	161.0	98.7	164.3	93.9	156.7	103.5	125.8	115.7	147.0	146.4	117.0	120.0	14
14	Ka-3-all	156.5	133.7	177.6	156.5	98.9	164.3	93.8	161.3	104.1	121.0	131.1	115.3	160.0	115.3	131.7	27
15	Ka-3-glu	159.3	132.7	176.7	155.8	98.4	163.4	93.4	160.6	103.7	120.6	130.5	114.8	160.6	114.8	130.5	27
16	Ka-3-gal	157.3	134.4	177.6	156.5	98.9	164.3	93.9	161.3	164.2	120.5	130.7	115.5	160.6	115.5	130.7	27
17	Ka-3-ara	156.3	133.2	177.5	161.0	93.6	164.7	98.5	156.7	103.9	120.6	130.7	115.3	159.7	115.3	130.7	57
18	Qu-3-glu	156.5	133.7	177.6	161.3	98.8	164.2	93.6	156.5	104.2	121.4	115.2	144.8	148.5	116.5	121.6	14
19	Qu-3-gal	156.3	139.8	177.5	161.2	98.6	164.0	93.4	156.3	104.0	121.3	115.2	144.7	148.5	116.2	121.8	14
20	Qu-3-ara	156.4	133.5	177.8	161.2	98.7	164.1	93.5	156.8	104.1	121.1	115.6	145.0	148.4	115.8	121.6	14
21	Qu-3-rha	156.4	134.4	177.7	161.2	98.6	164.0	93.5	157.0	104.2	121.0	115.4	145.1	148.3	115.8	121.0	14
22	Qu-3-rha, 3'OCH$_3$	156.2	133.4	177.5	161.3	98.8	164.2	93.7	156.4	104.2	121.2	113.9	149.5	147.1	115.3	122.1	14
23	My-3-gal	156.2	133.9	177.4	161.2	98.6	164.0	93.3	156.2	104.0	120.2	108.8	145.3	136.6	145.3	108.8	14
24	My-3-rha	156.5	134.5	177.8	161.4	98.7	164.1	93.6	157.4	104.2	119.8	108.3	145.8	136.5	145.8	108.3	14
Flavonol-O-diglycosides																	
a. with sugars linked to one oxycarbon																	
25	Ka-3-glu-(2"→1''')glu	156.4	133.1	177.5	161.2	98.6	164.0	93.6	156.4	104.2	121.1	130.6	115.2	159.7	115.2	130.6	14
26	Ka-3-glu-(6"→1''')rha	156.6	133.5	177.4	161.3	99.0	164.2	93.9	156.9	104.2	121.4	130.9	115.2	159.8	115.2	130.9	14
27	Ka-3-glu-(4"→1''')rha	157.3	134.4	177.6	156.5	98.9	164.3	93.9	161.9	104.2	120.5	130.7	115.5	160.0	115.5	130.7	27
28	Qu-3-glu-(6"→1''')rha	156.4	133.6	177.4	156.6	98.8	164.0	93.6	161.2	105.2	121.6	115.3	144.6	148.3	116.3	121.6	8
29	Qu-3-rut, 3'OCH$_3$	156.2	133.3	177.3	161.2	98.7	164.0	93.7	156.4	104.1	121.2	113.9	149.5	147.0	115.3	122.4	14

No.	Name**	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
30	Qu-7-rut, 4'OCH$_3$	147.3	136.3	176.1	160.4	98.9	162.8	94.5	155.8	104.8	123.4	115.2	146.3	149.6	112.2	119.9	14
31	Ka-3-gal-(6''→1''')glu	156.6	133.2	177.1	161.1	99.3	166.2	94.0	156.1	103.3	120.8	130.8	115.1	160.0	115.1	130.8	60a
b. with sugars linked to different oxycarbons																	
32	Ka-3,7-Glu	156.1	133.8	177.7	160.9	99.6	163.0	94.8	157.0	105.9	120.9	130.9	115.2	160.1	115.2	130.9	14
33	Ka-3-glu-7-rha	156.0	133.8	177.6	160.9	99.4	162.8	94.5	156.8	105.8	120.9	130.7	115.0	160.0	115.0	130.7	14
Flavonol-O-triglycosides																	
34	Ka-3-glu-(2'↓1''')glu, 7-glu	155.9	133.3	177.5	160.9	99.4	162.8	94.6	155.9	105.8	120.8	130.7	115.2	159.9	115.2	130.2	14
35	Ka-3-rut, 7-rha	156.0	133.7	177.6	160.9	99.4	161.7	94.6	157.1	105.8	120.8	130.7	115.1	159.1	115.1	130.7	14
36	Ka-3-rut, 7-glu	156.0	133.7	177.6	160.9	99.7	162.9	94.9	157.2	105.8	120.8	130.7	115.7	159.9	115.7	130.7	14
37	Ka-3-gla-(6''→1''')rha, 7-rha	156.0	133.6	177.6	161.6	99.5	160.8	94.8	157.1	105.7	120.7	131.1	115.2	160.1	115.2	131.7	13
38	Ka-3-rha-(2'')rha-(6'')glu	159.7	132.6	177.1	156.3	93.7	164.0	98.6	161.1	104.0	120.9	130.6	115.0	156.9	115.0	130.6	12
Flavanone-O-glycosides																	
39	Er-7-glu	78.3	42.2	196.2	163.4	95.7	166.6	94.8	162.8	101.7	129.4	114.2	145.1	145.6	115.3	117.8	58
40	Na-7-glu-(2'' →1''')rha	78.6	42.0	196.7	162.9	96.5	164.9	95.4	162.7	103.5	128.7	128.0	115.3	157.7	115.3	128.0	8
41	Ho-7-rut	78.4	42.0	196.7	163.0	96.7	165.2	95.8	162.5	103.5	131.2	114.3	146.7	148.1	112.7	117.8	8
42	Pi-7-glu-(2''→1''')rha	79.6	44.7	187.8	160.5	98.1	169.7	98.0	162.5	106.2	137.7	125.2	128.8	128.6	128.8	125.9	54

Table 14 ^{13}C Chemical Shifts for Acylated Flavonoid-O-glycosides*

No.	Name**	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
	Acylated flavone-O-glycosides																
1	Ac-7-(2''', 3'''-mbu)rut	163.3	104.3	182.4	157.5	100.9	164.4	95.0	161.5	105.9	123.1	128.7	114.9	162.8	114.9	128.7	55
2	Ap-3-(6''-ace)glu	162.8	103.2	182.0	157.0	99.7	164.3	94.9	161.4	105.5	121.1	128.5	116.0	161.2	116.0	128.5	66
3	Ap-4'-(2'', 6'',cou)glu	164.1	103.7	181.4	161.2	99.0	162.6	94.0	157.1	104.0	124.4	128.1	116.5	159.1	128.1	116.5	66b
	Acylated flavanone-O-glycosides																
4	Na-7-(6'' cou)-glu	78.6	42.0	197.2	163.0	96.3	165.0	95.5	162.6	103.3	128.6	128.4	115.1	157.7	115.1	128.4	63
	Acylated flavonol-O-glycosides																
5	Qu-3-(2'' gall)glu	156.3	132.8	177.1	161.3	98.8	165.2	93.6	156.3	104.1	121.1	115.3	145.0	148.6	116.1	122.1	66a
6	Qu-3-(6'' gall)gal	156.3	133.7	177.4	161.2	98.8	164.1	93.6	156.5	104.0	121.2	115.2	144.7	148.4	116.2	121.8	14
7	Ka-3-(6'' cou)glu	156.3	133.1	177.4	156.3	98.7	164.1	93.6	161.1	103.9	120.8	130.8	115.0	159.9	115.0	130.8	61
8	Ka-3-(6'' sin)glu,7-glu	155.8	133.4	177.4	160.8	94.5	155.8	94.5	155.8	105.8	121.0	130.6	115.1	159.9	115.1	130.6	14

Table 15 ^{13}C Chemical Shifts for Flavonoid-C-glycosides*

No.	Name**	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
	Flavone-C-monoglycosides																
1	Ap-8-glu	164.0	102.6	181.9	155.8	98.9	162.5	104.2	160.6	104.2	121.8	128.5	116.0	160.9	116.0	128.5	16
2	Ap-6-glu	163.8	102.9	181.9	156.9	108.8	163.8	94.2	161.3	103.5	121.2	128.4	116.3	160.6	116.3	128.4	16

No.	Name**	2	3	4	5	6	7	8	9	10	1'	2'	3'	4'	5'	6'	Ref
3	Lu-6-glu, 7-OCH_3	164.0	103.1	182.1	160.9	109.8	164.2	90.1	156.9	104.0	121.5	113.6	145.9	149.8	116.1	119.1	73a
	Flavone-C-diglycosides																
4	Ap-6,8-glu	163.9	102.6	182.2	155.0	107.6	161.4	103.7	161.3	105.3	121.5	129.0	115.9	158.7	115.9	129.0	16
5	Ap-6-glu, 8-ara	163.2	102.1	181.9	160.8	108.1	161.7	103.9	154.0	103.3	121.1	128.6	115.7	159.2	115.7	128.6	71
6	Ap-6-ara, 8-glu	163.8	102.4	182.0	160.9	108.0	161.1	104.4	154.8	102.9	121.4	128.5	115.7	158.4	115.7	128.5	71
7	Ap-6-gal, 8-ara	163.2	101.9	181.7	154.4	108.3	160.7	104.2	158.0	103.8	121.4	128.5	116.8	160.7	116.0	128.5	73
8	Lu-6,8-glu	165.8	104.1	183.8	157.2	108.1	163.9	105.0	160.1	105.8	123.6	115.2	146.4	150.5	117.5	121.3	16
	Flavone-C-,-O-glycosides																
9	Ap-6-C,7-O-glu	164.4	103.4	182.3	156.7	110.7	162.6	94.0	161.5	105.2	121.1	128.8	116.3	159.6	120.5	127.7	16
10	Ge-5-O,6-C-glu	161.4	103.0	182.3	156.9	90.8	161.4	104.8	159.8	109.5	121.0	128.4	116.0	164.0	116.0	128.4	59

* Signals due to the aglycone moiety only are included here.

** Flavonoid abbreviations: Ap (Apigenin), Lu(Luteolin), Ka(Kaempferol), Qu(Quercetin), My(Myricetin), Ac(Acacetin), Di(Diosmetin), Er(Eriodictyol), Na(Naringenin), Ho(Hoeriodictyol), Pi(Pinocembrin), Ge(Genkwanin).

Sugar abbreviations: glu(Glucose), gal(Galactose), rha(Rhamnose), all(Allose),ara(Arabinose),rut(Rutinose),

Acid abbreviations: Mbu(2-methylbutyric acid), Cou(Coumaric acid), gall(Gallic acid), sin(Sinapic acid) Ace(acetic acid).

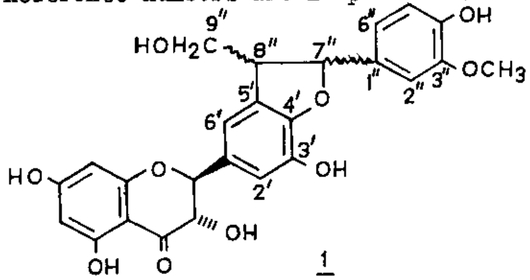
Pseubap$^+$ = Pseudobaptisin(3',4'-OCH_2O-Isoflavone-7-O-rutinoside)

Table 16 ^{13}C Chemical Shifts for Flavono-lignans

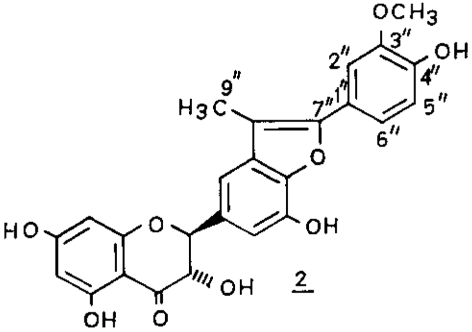
Carbon No.	1(87)*	2(87)	3(88)	4(86)	5(88)	6(88)	7(88)	8(88)
2	83.5	83.5	164.7	82.0	164.2	164.3	164.1	164.5
3	72.1	71.9	103.8	71.0	103.8	103.8	103.9	104.8
4	197.3	197.6	181.7		181.6	181.7	180.4	180.8
5	163.6	163.3	157.4	162.5	157.3	157.3	157.7	157.3
6	96.6	96.1	99.0	95.5	98.5	98.9	98.8	97.1
7	167.0	166.8	161.6	165.9	161.4	161.4	161.5	161.3
8	95.2	95.0	94.0	94.5	93.9	94.0	93.8	96.8
9	162.6	162.5	164.1	161.6	162.8	163.0	156.9	161.3
10	100.5	100.5	103.4	99.8	103.8	103.8	103.9	104.8
1'	129.0	122.0	123.6	142.9	123.6	122.3	127.1	120.3
2'	115.3	109.8	116.6	146.2	119.3	104.1	112.1	113.7
3'	147.4	150.9	130.7	146.2	116.7	149.0	145.3	147.2
4'	140.4	141.6	141.6		147.2	136.0	147.3	148.2
5'	129.9	122.0	145.2		143.6	144.3	115.5	119.2
6'	115.8	110.0	114.4		114.6	108.1	113.4	133.9
1"	132.6	132.5	132.0		127.0	127.0	122.1	132.4
2"	110.2	110.4	110.4		110.9	112.0	113.2	112.3
3"	147.6	147.8	147.8	146.8	147.7	147.7	147.8	147.9
4"	147.4	147.1	147.7	142.5	147.0	147.2	147.2	147.6
5"	115.1	115.9	115.7		115.4	115.4	132.5	115.7
6"	118.7	119.7	119.2		120.6	120.6	119.2	127.2

Carbon No.	1(87)*	2(87)	3(88)	4(86)	5(88)	6(88)	7(88)	8(88)
7"	87.3	141.7	87.9		78.1	78.3	77.8	40.9
8"	53.7	109.5	52.8		76.4	75.7	76.1	35.2
9"	63.2	9.3	62.9		59.6	59.9	59.8	69.2

*Reference numbers are in parentheses.



1



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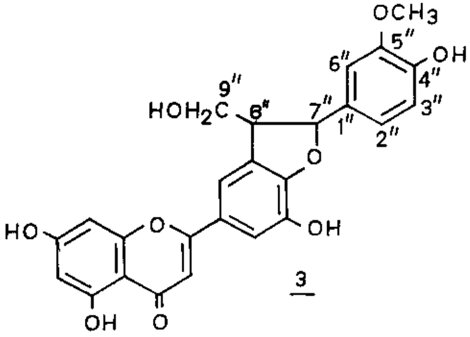

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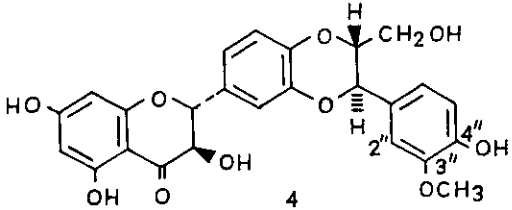

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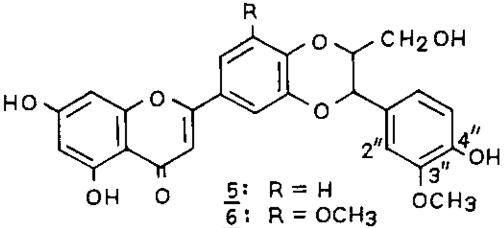
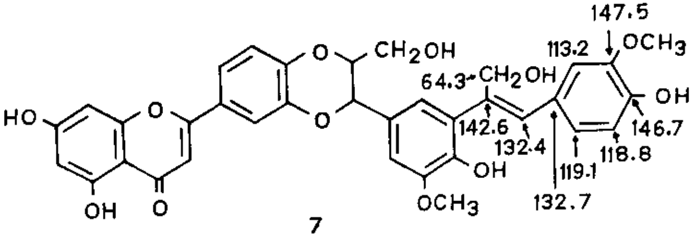


5: R = H
6: R = OCH3



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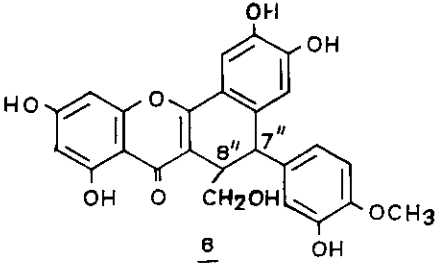

8

Table 17 ^{13}C Chemical Shifts of the three Carbons of Ring C*

Category	C-2	C-3	C-4 a^{+}	 b^{+}
Flavanones	75.0 - 80.3	42.5 - 44.6	188.6 - 194.6	195.0 - 198.0
Isoflavanones	70.0 - 72.0	44.0 - 45.0	190.0 - 192.0	197.0 - 198.0
Flavanonols	83.0 - 84.5	71.0 - 73.5		195.0 - 198.0
Flavones	160.0 - 165.5	104.0 - 111.8	176.3 - 178.3	181.0 - 183.5
Isoflavones	149.8 - 156.5	123.3 - 125.9	174.5 - 178.6	181.0 - 182.5
Flavonols	146.0 - 148.5	135.0 - 138.0	172.5 - 174.0	175.0 - 177.0
	C-α	C-β	C=O	
Chalcones	116.6 - 128.5	136.9 - 145.4	188.6 - 194.6	
	C-2	C-3	=CH	
Aurones	146.0 - 147.9	182.5 - 183.0	111.5 - 112.0	
Isoaurones	168.6 - 168.8	137.0 - 140.7	137.0 - 140.7	

*The chemical shift ranges for flavans, isoflavans, flavan-3-ols, flavan-3,4-diols and dihydrochalcones, could not be included here since the examples reported so far are insufficient for generalisation.

a^{+} and b^{+} represent C-4 chemical shifts with and without chelation respectively in each class.

Table 18 ^{13}C Chemical Shifts of Ring A and C carbons in 5,7-dihydroxy flavonoids*

	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Ref
Flavanone	78.3	42.2	196.2	163.4	95.7	106.6	94.8	162.8	101.7	34
Flavanonol	83.1	71.7	197.1	163.5	96.1	166.8	95.1	162.5	100.6	8
Isoflavanone	70.7	44.6	198.0	164.2	96.1	167.0	95.0	163.5	102.4	35

	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Ref
Flavone	165.49	104.33	183.18	158.67	95.57	164.93	100.97	164.09	105.06	9
Flavonol	148.32	136.73	176.71	157.48	94.99	164.52	99.60	161.36	104.39	9
Isoflavone	154.01	123.88	181.37	163.70	99.73	164.73	94.32	158.82	106.05	21

*Ring B carbon resonances could not be included here because the data of an identical set of ring B carbons in all the groups were not available.

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