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PLANT POLYPHENOLS—XII.

THE OCCURRENCE OF TRICIN AND OF GLYCOFLAVONES IN GRASSES*

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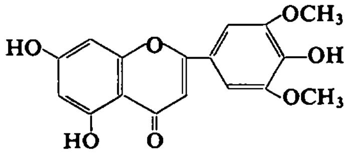
Abstract—Traces of free tricin have been detected in the leaves of sixteen grasses and two tricin glucosides (one being the 5-monoglucoside) have been isolated from *Triticum dicoccum*, *T. monococcum* and *T. polonicum*. However, the major phenolic constituents of grasses are glycoflavones and eight, present in *Avena* and *Triticum*, have been studied in detail. One is saponarin, another lutonaretin and the remainder are apigenin or luteolin derivatives having carbon–carbon linked sugars, which differ from those of vitexin and saponaretin. A report that tricin occurs free in lucerne leaves could not be confirmed; instead, two tricin glucuronides and chrysoeriol 7-glucuronide were isolated.

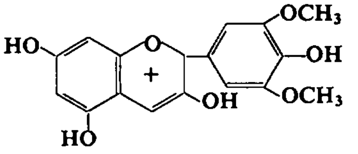
INTRODUCTION

The flavone tricin (I) is of especial interest phytochemically because, although it is structurally related to the widely occurring anthocyanidin, malvidin (II), and to the cinnamic acid, sinapic acid (III), it is itself of rare occurrence. It was first isolated in 1934 from the rust-resistant wheat *Triticum dicoccum* cv. 'Khapli',[1] and was later identified[2] as the muscle-inhibiting factor in the juice of lucerne, *Medicago sativa* (Leguminosae). It has also been isolated from another plant of the Gramineae, rice *Oryza sativa*,[3] and occurs in the free state in seeds of *Orobanche ramosa* L. (formerly *Phelypaea ramosa* Tourn. ex Des.) (Scrophulariaceae).[4,5]



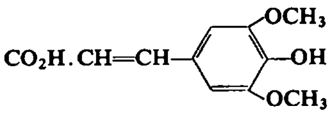
Tricin

(I)



Malvidin

(II)



Sinapic acid

(III)

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* Part XI, J. B. Harborne, *Phytochemistry*, 3, 151 (1964).

[1] J. A. Anderson, *Canad. J. Res.* 9, 80 (1933).

[2] W. S. Ferguson, de B. Ashworth and R. A. Perry, *Nature*, 163, 606 (1949); 166, 116 (1950).

[3] S. Kuwatsuka and Y. Oshima, *J. agric. chem. Soc. Japan* 35, 71 (1961).

[4] C. Izard and J. Masquelier, *C. R. Acad. Sci. Paris* 246, 1454 (1958).

[5] J. B. Harborne, *Chem and Ind.* 1950 (1958).

It has been assumed, with little experimental evidence, that tricin is a major and characteristic phenol of the grasses and it has been reported[6] to occur consistently in the leaves. Preliminary attempts to isolate tricin from crude or acid-hydrolysed extracts of a number of grasses were, however, not successful[7] and it seemed possible that this was because it occurred as a glycoside, which was unusually stable to hydrolysis. For this reason and because no glycoside of tricin had been reported in the known plant sources, a re-investigation of the flavone glycosides of grasses has been carried out. The report[2] that tricin occurs free in lucerne has also been examined.

RESULTS

Tricin and its Glycosides in Wheat and Lucerne Leaves

In preliminary studies using established procedures,[6,8] neither tricin nor its derivatives could be detected chromatographically in crude or acid-hydrolysed extracts of wheat leaves. The difficulty appeared to be that (*a*) the characteristic colour reactions of tricin were masked by other flavonoid components and (*b*) there was very little present. However, when fresh leaf extracts were chromatographed in water, tricin-like material appeared near the origin, being separated from the major flavonoids, which were mobile. This procedure was applied to *Triticum dicoccum* cv. 'Khapli' (from two different botanical sources) and to six other *Triticum* species and at least seven flavones were found to be variously present (Table 1). The band T1 (showing, characteristically of tricin, a yellow fluorescence in u.v. light with ammonia vapour) was present in relatively low concentration. It was isolated by chromatography on No. 3 paper separately from *T. dicoccum*, *T. monococcum* and *T. polonicum* and, in each case, when chromatographed in butanol–acetic acid–water, T1 separated into three

TABLE 1. SURVEY OF THE FLAVONES OF *Triticum* SPECIES

	R_f values on Whatman No. 1 paper* in water of					
Triticum species	Tricin-like band	Glycoflavones				
Dicoccum cv. 'Khapli'†	0·09(T1)	0·16(T2)	0·29(T3)	0·46(T4)	0·56(T5)	0·71(T7)
Dicoccum	0·09	0·18	0·31	0·47	0·58	
Dicoccoides	0·08		0·32		0·58	
Monococcum	0·01, 0.07(T1)		0·32(T6)		0·56	
Polonicum	0·08(T1)	0·18	0·30(T6)			
Spelta		0·14	0·28	0·45	0·57	0·76
Turgidum	0·09	0·17	0·27	0·44	0·57	0·76
Vulgare Vill. (= *T. aestivum* L.)	0·08	0·18	0·30	0·47	0·59	

* Colours in ultraviolet in absence and presence of ammonia: tricin-like band, dull brown → intense fluorescent yellow; glycoflavones, dull brown → bright yellow green.

† Two sources of 'Khapli', from India and Toulouse, were examined and were identical; of six other forms of *T. dicoccum* examined, only two had the tricin-like band.

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[6] E. C. BATE-SMITH, *Sci. Proc. R. Dublin Soc.* **27**, 165 (1956).

[7] T. SWAIN, private communication, and our own preliminary experiments.

[8] J. B. HARBORNE, *J. Chromatography* **2**, 581 (1959).

components, T1.1, T1.2 and T1.3 (Table 2). T1.1 was identified as tricin by co-chromatography in six solvent systems with authentic material and by spectral measurements. Thus Anderson's original report of tricin in wheat[1] is confirmed. T1.2 was identified as tricin 5-monoglucoside, on the basis of its spectral characteristics, hydrolysis products and R_f values. That it is a monoside follows from the fact that no intermediate could be detected during its hydrolysis with β-glucosidase. That it is a 5-glycoside follows from its spectral properties (Table 2) and the fact that its fluorescence on paper in u.v. light (pale blue going to yellow with ammonia) are quite different from those of the 7-glucuronide, isolated from lucerne (see below). T1.3 was not present in sufficient amount for detailed analysis, but its properties (Table 2) indicate that it may be a 5-glucosylglucoside of tricin.

TABLE 2. PROPERTIES OF TRICIN AND ITS DERIVATIVES

Compound	R_f values in† BAW	H_2O	BEW	PhOH	Forestal
Tricin	0·87	0·00	0·74	0·91	0·76
T1.1	0·87	0·00	0·74	0·91	0·76
T1.2 from *Triticum*	0·23	0·00	0·30	0·89	—
T1.3	0·08	0·05	0·17	0·78	—
M1	0·29	0·01	0·16	0·71	—
M2 from *Medicago*	0·36	0·33	0·26	0·65	—
M3	0·22	0·30	0·07	0·15	—
5,7,3′,4′-tetraOH,5′-OMe flavone	0·65	—	—	0·76	0·51
5,7,3,4′,5′-pentaOH flavone	0·56	—	—	0·28	0·37

Spectral properties: λ_{max} in 95% EtOH (mμ) ‡

Compound	Alone Band I	Alone Band II	+2 N NaOH Band II	+5% $AlCl_3$ Band II	+Satd. NaOAc Band I	+NaOAc/H_3BO_3 Band II
Tricin	≈248, 269	355	420	360, ≈379	270	354
T1.1	≈248, 269	355	420	360, ≈379	270	354
T1.2	≈245, 262	351	415	352, ≈400	265	354
M1	≈249, 269	357	403	370, 385	269	357
M2	254, 269	351	397	354, ≈380	269	350
5,7,3′,4′-tetraOH,5′-OMe flavone	248, 270	355	432	≈367, 395	272	380
5,7,3,4′,5′-pentaOH flavone	250, 269	356	unstable	≈365, 398	270	382

Hydrolysis Products

Compound	Products and ratios	Identified as
T1.2	Tricin and glucose	Tricin 5-glucoside
T1.3	Tricin and glucose	Tricin 5-glucosylglucoside (?)
M1*	Tricin (1·0) and glucuronic acid (0·87)	Tricin 7-glucuronide
M2*	Chrysoeriol and glucuronic acid	Chrysoeriol 7-glucuronide
M3*	Tricin and glucuronic acid	Tricin 7-glucuronosylglucuronide (?)

† All, except T1.2 and T1.3 which were blue, fluoresced dull brown in u.v. light; all going bright yellow in the presence of HN_3.

* Hydrolysed by β-glucuronidase.

‡ ≈ = inflection.

In Table 2 are included the spectral properties and R_f values of two tricin derivatives, namely 5,7,3′,4′,5′-pentahydroxyflavone and its 5′-monomethyl ether, which were prepared by demethylation of tricin with pyridinium chloride. Neither of these compounds were, however, detected in grasses during the present studies.

Since lucerne leaves were reported[2] to contain free tricin, it seemed of interest to re-examine them using the methods developed during the wheat studies. Chromatography in water of a leaf extract showed the presence of a tricin-like component as one of the major constituents. On purification, this band yielded no free tricin but gave a single glycoside M1, of which the properties are recorded in Table 2; it was readily identified as tricin 7-glucuronide. This substance has not been previously described, but the 7-glucuronides of apigenin, luteolin and chrysoeriol are all known.[9] Indeed, a second flavone, M2, in lucerne was identified as chrysoeriol 7-glucuronide, by means of co-chromatography with authentic material isolated from flowers of *Antirrhinum majus*.[9] A third, very minor component, M3 (Table 2), was also found in lucerne; insufficient material was available for complete identification but it appeared to be a glucuronosylglucuronide of tricin.

Glycoflavones of Avena *and* Triticum

Eight glycoflavones were isolated from leaf extracts of *Avena* and *Triticum* species. Five of them (T2.1, T2.2, T2.3, T3 and T5) were obtained from *Triticum dicoccum* cv. 'Khapli' and most are probably also present in other *Triticum* species, since there is good correspondence in the R_f values of the glycoflavones from the various sources (see Table 1). However, in one case, further investigation showed that compounds with similar R_f values in water were not identical. Thus, the band corresponding to T3 in *T. dicoccum* was isolated from *T. polonicum* and *T. monococcum* and found to be different from T3; it was therefore designated T6. The other two glycoflavones, A1 and A2, were obtained from oat leaves, *Avena sativa* cv. 'Blenda'. A2 was also detected chromatographically in *Avena nuda*, *A. sterilis*, *A. byzantina*, *A. fatua*, *A. brevis* and *A. strigosa*, A1 also being present in the first four of these species.

That all eight compounds were glycoflavones followed from comparison of spectral properties, R_f values and hydrolysis products with those of known glycoflavones (see Table 3). Furthermore, like the glycoflavones isolated from *Hordeum vulgare*,[10] they were both difficult to purify and rather unstable to oxidation. Only three, T2.1, T3 and T6, were identified as known compounds. T2.1 was found to be lutonaretin; it is possible that it occurs free in wheat leaves but it is just as likely that it was produced from the major glycoflavone T5 by hydrolysis during extraction. T6 was identified as saponaretin 7-*O*-glucoside by direct comparison with saponarin isolated from *Saponaria officinalis*.[11] A third compound, T3, was found to be similar to or identical with flavonoid B, a glycoapigenin found in wheat germ by King.[12] Like flavonoid B, it was inter-convertible with its isomer, flavonoid C. The other five compounds are all new glycoflavones based on apigenin or luteolin. They appear to lack *O*-glycosyl links because: (*a*) their spectra undergo bathochromic shifts on addition of various inorganic ions (Table 3), (*b*) they were unaffected by treatment with β-glucosidase or anthocyanase, and (*c*) the products obtained by methylation and subsequent hydrolysis of T5, A1 and A2 contained no free hydroxyl groups (their spectra were the same in both neutral and

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[9] J. B. HARBORNE, *Phytochemistry* **2**, 327 (1963).

[10] M. K. SEIKEL, A. J. BUSHNEL and R. BIRZGALIS, *Arch. Biochem. Biophys.* **99**, 451 (1962).

[11] G. BARGER, *J. Chem. Soc.* **89**, 1210 (1906).

[12] H. G. C. KING, *J. Sci. Fd Agric.* **27**, 446 (1962).

TABLE 3. PROPERTIES OF GLYCOFLAVONES OF GRASSES

Compound		R_f values* in BAW	H_2O	BEW	PhOH
T2.1	from *Triticum*	0·41	0·09	0·41	0·51
T2.2		0·18	0·23	0·14	0·39
T2.3		0·14	0·09	0·09	0·38
T3		0·31	0·28	0·28	0·73
T5		0·37	0·51	0·35	0·41
T6		0·38	0·33	0·45	0·60
A1	from *Avena*	0·45	0·54	0·55	0·82
A2		0·47	0·57	0·55	0·80

Spectral properties: λ_{max} in 95% EtOH (mμ) ||

Compound	Alone Band I	Alone Band II	+2 N NaOH Band II	+5% $AlCl_3$ Band II	+Satd. NaOAc Band I	+NaOAc/H_3BO_3 Band II
T2.1	259, 271	352	413	358, 387	273	379
T2.2	≈ 262, 272	353	414	365, 392	283	385
T2.3	≈ 265, 272	353	417	365, 398	282	383
T3	274	337	403	343, 380	283	373
T5	258, 271	352	415	≈ 370, 389	273	380
T6	272	337	398	344, 380	272	338
A1	272	337	403	342, 385	278	343
A2	272	337	402	344, 381	280	346

Compound	Products† of acid treatment	Identified as
T2.1	Lutexin, no sugar and unchanged T2.1	Lutonaretin
T2.2 T2.3	Unidentified "aglycones", no sugar	Luteolin *C*-glycosides
T3	Flavonoid B (flavonoid C), no sugar	Apigenin *C*-glycoside
T5	Lutonaretin (lutexin) and rhamnose	Luteolin *C*-rhamnosylhexoside
T6	Saponaretin (vitexin) and glucose	Saponarin
A1	Vitexin (saponaretin) and rhamnose	Apigenin *C*-rhamnosylglucoside
A2	Saponaretin (vitexin) and arabinose	Apigenin *C*-arabinosylhexoside

Products of methylation and hydrolysis

	R_f values in BAW	PAW	15% HOAc	Colour, in ultraviolet	λ_{max} 95% EtOH	+2 N NaOH
T5	0·52	0·90	0·72	blue fluorescence	242, ≈ 262, 333	242, ≈ 262, 332
A1	0·47	0·86	0·71		266, 322§	266, 324
A2	0·74	0·91	0·81		262, 324§	262, 324

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* All fluoresced dull brown in u.v. light going yellow or yellow–green in the presence of NH_3.

† Minor product of acid hydrolysis is shown in parentheses.

‡ R_f values were as follows (value for vitexin given in parentheses): in BAW, 0·15 and 0·08 (0·41); in H_2O, 0·14 and 0·03 (0·06); in BEW, 0·13 and 0·13 (0·47); and in PhOH, 0·38 and 0·30 (0·63).

§ These spectral maxima were not changed on addition of powdered sodium acetate to the cell solution.

|| ≈ = inflection.

alkaline media, cf. Table 3). T2.2 and T2.3 appear to be a pair of related glycoluteolin derivatives in which the carbon–carbon linked sugar is either quite different from those present in lutexin and lutonaretin; or else is linked to a different position in the flavone nucleus. Flavonoid B, and its isomer flavonoid C, probably differ in a similar way from vitexin and saponaretin. The other three have two sugar residues attached in the 8-position, and can be provisionally formulated as follows: T5 is a luteolin 8-*C*-rhamnosylhexoside,* A1 an apigenin 8-*C*-rhamnosylglucoside and A2 is an apigenin 8-*C*-arabinosylhexoside.*

A Survey of Some Grasses

Leaf extracts of representatives of thirteen grass genera were surveyed for the presence of tricin and glycoflavones. Extracts were run in water and, in most cases, the major flavonoid bands were cut out, eluted and hydrolysed. The results of this survey are summarized in Table 4. Glycoflavones were found to be present in eleven out of the thirteen; they were further identified as derivatives of glycoapigenin or glycoluteolin in five cases. Nine of the samples contained a tricin-like component, similar to the band T1 noted in *Triticum* and it seems reasonable to assume that tricin, either free or combined, is present in all these nine species. The band in *Oryza sativa* was purified and found to be identical with T1.2 (i.e. tricin 5-glucoside). Although tricin itself has previously been identified in rice, the glycoside present was not positively identified.[13]

TABLE 4. SURVEY OF FLAVONES IN LEAF EXTRACTS OF GRASSES

Species	Presence/absence of tricin-like band of low R_f in H_2O	R_f values of other flavones in H_2O	Products of acid hydrolysis of main flavone bands
Agrostis canina	–	0·33, 0·46	Lutonaretin and lutexin
Anthephora elegans	–	0·09	Not studied
Beckmannia erucaeformis	+	0·09	Not studied
Brachypodium sylvaticum	–	0·09, 0·18	Not studied
Briza media	+	0·09, 0·19	Saponaretin and vitexin
Bromus ciliatus	+	0·34	Tricin*
Festuca pratensis†	+	0·33‡	Quercetin
Helictotrichon pubescens (= *Avena pubescens* Huds.)	+	0·08, 0·24	Not studied
Oryza sativa	+	0·03, 0·19, 0·41, 0·51	Lutonaretin, lutexin, saponaretin and vitexin
Poa compressa	+	0·09, 0·18	Lutonaretin and lutexin
Sorghastrum nutans	+	0·09	Not studied
Stipa calamagrostis	–	0·09	Lutonaretin and lutexin
Tripsacum dactyloides	+	0·09	Not studied

* Aglycone from the main component of *Bromus*, which had R_f 0·04 and tricin-like colour reaction.

† *Festuca* also has a component R_f 0·11 in H_2O with tricin-like colour reaction.

‡ Identified as rutin by co-chromatography in five solvent systems; it also gave quercetin on β-glucosidase or anthocyanase treatment (none of the flavone bands obtained from other species was affected by these enzymes).

* The term 'hexoside' is used here to indicate the as yet unidentified sugar unit present in saponaretin and lutonaretin.

[13] I. NAGAI, G. SUZUSHINO and Y. SUZUKI, *Jap. J. Breeding* **10**, 247 (1960).

One plant, *Festuca pratensis*, was exceptional in lacking glycoflavones and having instead the common flavonol glycoside, rutin. This appears to be the first flavonol glycoside to be identified in a grass. Bate-Smith[14] has also noted that flavonols occur but rarely in grass leaves.

DISCUSSION

In an earlier survey, Bate-Smith[6] observed that tricin occurred consistently as an aglycone in hydrolysed extracts of the grasses and the present results confirm that it is of regular occurrence in this family. However, it seems unlikely that it occurs extensively in the free state, as suggested by earlier workers. It is true that traces of free tricin have been detected in the leaves during the present work, but these could have arisen by hydrolysis of glycosides during extraction. The great majority of flavonoids occur in leaf tissue combined as glycosides[15] and two glycosides of tricin have now been identified in *Triticum dicoccum* and others are probably present in other members of the Gramineae (see footnotes to Table 4). Further, re-examination of lucerne shows that tricin is present, not in the free state, but in combination with glucuronic acid. In the original work on lucerne, no steps were taken to avoid enzymic hydrolysis and sufficient β-glucuronidase is presumably present in lucerne juice to bring about hydrolysis of the combined tricin.

Although tricin, in combined form, is a characteristic grass flavone, it is only a minor constituent of most species studied; the major phenols are glycoflavones based on apigenin and luteolin. Already, Seikel[10] has found three glycoflavones in barley leaves, *Hordeum vulgare*, and King[12] two in wheat germ. In all, glycoflavones have now been detected in fifteen genera of the Gramineae so that they are another characteristic chemical feature of the family. The glycoflavones of *Avena* and *Triticum* are unusual in occurring, not as *O*-glycosides, but as 8-*C*-disaccharides. Only one compound of this type has been described earlier; this is a lutonaretin xyloside found in *Adonis vernalis* by Hörhammer and Wagner.[16] Further work on these 8-*C*-diglycosides can hardly be carried out until the exact structure of the 8-monoglycosides are known. From recent studies,[17,18] it is almost certain that vitexin is apigenin 8-*C*-glucoside, but the structure of saponaretin has yet to be determined.

The recognition of tricin or tricin-like compounds in sixteen out of twenty grass genera examined suggests that it is widespread in the family. Such a sample is however a small one, when it is remembered that the Gramineae contains some 450 genera and 4500 species. By contrast, tricin does not appear to be present at all regularly in the other two families in which it has found. Thus, it has not been detected in any member of the Leguminosae other than *Medicago*. For example, it was not found during a recent wide survey of the leaf phenolics of species belonging to the genera *Lotus*, *Pisum*, *Lathyrus*, *Phaseolus* and *Vicia*.[19] In the case of the Scrophulariaceae, tricin was first found in the seed of the tobacco parasite, *Orobanche ramosa*. Seeds of ten other *Orobanche* species have now been studied (see Experimental) but only one other species, *O. arenaria*, contained tricin.

Finally, it is interesting to note of the flavones of grasses, that apigenin and luteolin occur (apparently) exclusively as *C*-glycosides, whereas tricin is found only as an *O*-glycoside. It

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[14] E. C. Bate-Smith, unpublished work.

[15] J. B. Harborne, in *Biochemistry of Phenolic Compounds*, Ch. 4, Academic Press, in press.

[16] L. Hörhammer and H. Wagner, in *Chemistry of Natural Phenolic Compounds* (Edited by W. D. Ollis), p. 185. Pergamon Press, Oxford (1961).

[17] C. B. Rao and V. Venkateswarlu, *J. sci. ind. Res.* **21B**, 313 (1962).

[18] B. H. Koeppen, *Chem. and Ind. (Rev.)* 2145 (1962).

[19] J. B. Harborne, unpublished work.

remains to be seen whether the common flavones and tricin have separate biosynthetic pathways, since a *C*-glycoside of tricin may yet be isolated.

EXPERIMENTAL

Plant sources. Avena and *Triticum* species were grown from seed both in soil in the glasshouse and in damp vermiculite, for 4–8 weeks. Leaf material of other genera were kindly provided by the London University Botanical Supply Unit, Englefield Green.

Authentic materials. Samples of flavonoids A and B and of tricin were generously donated by Dr. H. G. C. King. Specimens of lutonarin, vitexin and saponarin were kindly provided by Dr. M. K. Seikel. 5,7,3′,4′-Tetrahydroxy-5′-methoxyflavone and 5,7,3′,4′,5′-pentahydroxyflavone were prepared by demethylating tricin with pyridinium chloride for 5 hr at 140–150° under N_2. The crude product was extracted with ethyl acetate, and the extract concentrated and chromatographed in PAW, when the monomethyl ether (R_f 0·66) was separated from the pentahydroxyflavone (R_f 0·54).

Paper chromatography. The following solvent mixtures were used: BAW, *n*-butanol–acetic acid–water (4:1:5, top layer); BEW, *n*-butanol–ethanol–water (4:1:2·2); PHOH, phenol satd. with water; PAW, *n*-propanol–acetic acid–water (1:1:1); and Forestal, acetic acid–conc. HCl–water (30:3:10).

Extraction and purification. Fresh leaf was extracted with hot MeOH and the extracts concentrated to a small volume. Chlorophyll was removed by centrifugation and by washing with pet. ether. Flavones in the clear pale yellow concentrates were then separated and purified by paper chromatography in water, followed by BAW, 15% acetic acid and BEW.

Identifications. These were carried out by well-established procedures.[8] For acid hydrolysis, *O*-glycosides were hydrolysed with 2 N HCl at 100° for 40 min. For *O*-glycosides of *C*-glycosides, hydrolysis was carried out under similar conditions for up to 4 hr, but samples were taken every 5 min for the first 45 min to determine which of the two possible *C*-glycosides was first formed from the *O*-glycoside. In all cases, the actual *C*-glycoside (e.g. vitexin) appeared first in greater amount and eventually an equilibrium mixture of the two isomers (e.g. vitexin–saponaretin) was obtained. Enzymic hydrolyses were carried out in sodium acetate buffer (pH 5·0) at 37° for 4 hr at an enzyme concn. of 1 mg/ml. For complete methylation and hydrolysis, the flavone was treated with acetone, K_2CO_3 and dimethyl sulphate at the b.p. for 4 hr. The acetone extract was evaporated to dryness and the residue was heated with 2 N HCl at 100° for 30 min. The product was purified by chromatography in 15% HOAc and then in BEW.

Survey of Orobanche *seeds.* Seeds were crushed in a mortar and the debris extracted with boiling EtOH for 1 hr. The solutions were concentrated and the extracts examined by paper chromatography in BAW and water. Only *O. ramosa* and *O. arenaria* contained tricin, which was identified by co-chromatography in five solvent systems and by spectral measurements. Species which lacked tricin (or any flavone) were *amythystea, crenata, cumana, hederae, lucorum, minor* and *rapumgenistae*. All species contained one or two chlorogenic acid-like components.