Phytochemistry, 1976, Vol. 15, pp. 215–218. Pergamon Press. Printed in England.

THE FINAL STRUCTURE OF ROBININ AND BIOROBIN AND THEIR TOTAL SYNTHESIS

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(*Received* 13 *June* 1975)

Key Word Index—*Robinia pseudacacia*; Leguminosae; robinin; flavonoid triglycoside; synthesis; kaempferol glycosides.

Abstract—Robinin has been proved by total synthesis and by methylation analysis using GC-MS to be kaempferol-3-*O*-(6-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside)-7-*O*-α-L-rhamnopyranoside and not, as claimed by Maksjutina *et al.*, a mixture of 4 glycosides containing the 7-*O*-rhamnosyl moiety in the α- and β-furanoside as well as in the α- and β-pyranoside forms. The assumption that the 3-*O*-rhamnosido-galactose moiety contained furanoid rings was also disproved.

Robinin, the main flavonoid of the leaves of *Robinia pseudoacacia* was isolated by Zwenger and Dronke as early as in 1861 [1]. Substances having the same composition, optical rotation and the characteristic double mp (195–197° from water and 249–250° from EtOH) have been isolated from several other plants [2–4], among them from *Robinia viscosa* and a *Cheiranthus* species by Maksjütina as well as from another *Cheiranthus* species and *C. allionii* by Maksjutina *et al.* [5–8]. The identity of the above mentioned products both between themselves and with "robinins" isolated by earlier investigators [9,10] has been demonstrated [11].

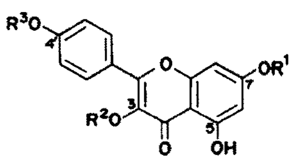
After various contributions [9,12–14], the structure of robinin was finally elucidated by Zemplén and Bognár in 1941 [10] and found to be **1** [15]. This structure was later confirmed also by Shimokoriyama [19].

Examining samples of robinin isolated from *Cheiranthus* [7] and *Robinia viscosa* [5], Maksjutina and her co-workers came to the following two conclusions: First, robinin is a mixture of 4 isomeric glycosides (**2–5**) differing in the structure of the 7-*O*-rhamnosyl moiety, being present in the α- and β-pyranoside and furanoside forms. Second, in contrast to Zemplén's suggestion [10,16] the saccharide moiety is not robinobiosyl, but 6-*O*-β-L-rhamnofuranosido-β-D-galactofuranosyl [20]. These conclusions were based on the IR spectra and molecular rotations of glycosides obtained by partial hydrolysis of robinin.

In this paper we wish to present synthetic and analytical evidence for the homogeneity of robinin and for the correctness of the original structure proposed by Zemplén and Bognár (**1**) [10].

Partial hydrolysis of robinin with 0·16% HCl, as described by Maksjutina *et al.* [5,7] gives rise to kaempferol-7-*O*-rhamnoside. In our hands [21] this method yielded a crystalline, chromatographically homogenous specimen having the same mp (229–231°) and optical rotation [22] as kaempferol-7-*O*-rhamnoside obtained by partial enzymic hydrolysis [14] and nearly the same mp as the kaempferol-7-*O*-rhamnosides isolated from *Celastrus orbiculata* Thunb [23], and from *Exocarpus cupressiformis* Labill [24]. None of the three kaempferol-7-*O*-rhamnosides isolated by Maksjutina *et al.* [5,7] from the partial hydrolysate of robinin and claimed to be the α- and β-furanosides and the α-pyranoside resp. possessed however these characteristics. In order to determine the ring size of the sugar moiety, total methylation of our kaempferol-7-*O*-rhamnoside was carried out by the Hakomori-Lindberg method [25] giving after hydrolysis, reduction and acetylation as the only product 2,3,4-tri-*O*-methylrhamnitol diacetate, indicating that rhamnose was present exclusively in the pyranose form. The α-configuration and anomeric homogeneity of our product was proved by synthesis. Coupling of kaempferol-4′-benzyl ether (**7**) [26] with 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide [27] gave after saponification to **8** and subsequent catalytic debenzylation kaempferol-7-*O*-α-L-rhamnopyranoside (**6**) which was found to be identical with the product of partial acid hydrolysis. This implies that the kaempferol-7-*O*-rhamnoside isolated from *Celastrus orbiculata* [23] is also an α-pyranoside [28]. The pyranoside structure of **6** follows from the constitution of the glycosyl halide, unaltered during the coupling reaction. The assignment of the α-configuration to **6** is

based partly on its large negative rotation [29] ($[\alpha]_D^{25}$ − 130°; phenyl-α-L-rhamnopyranoside: $[\alpha]_D^{18}$ − 106°; phenyl-β-L-rhamnopyranoside: $[\alpha]_D^{18}$ +87·5°) and on NMR data. The ^{1}H-NMR-spectrum of the hexaacetate of **6** was well resolved when recorded in C_6D_6 and could be fully assigned with the aid of double resonance experiments (see Experimental). The coupling constant of H-1 and H-2, (found 2·0 Hz in **6** −hexaacetate) is uninformative for rhamnose in the favoured 1C conformation, since the disposition of the protons of interest is *gauche* in both anomers. The spectrum of **6** however was superimposable in the region of non-aromatic protons to that of tri-*O*-acetyl-α-phenylrhamnopyranoside [29]. The ^{13}C chemical shift of C_1 is unfortunately of no diagnostic value for the determination of the anomeric configuration of sugars in the *manno*-series [30].



(1) R¹ = α-L-Rha*p*; R² = 6-*O*-α-L-Rha*p*-β-D-Gal*p*; R³ = H
(2) R¹ = α-L-Rha*p*; R² = 6-*O*-β-L-Rha*f*-β-D-Gal*f*; R³ = H
(3) R¹ = β-L-Rha*p*; R² = 6-*O*-β-L-Rha*f*-β-D-Gal*f*; R³ = H
(4) R¹ = α-L-Rha*f*; R² = 6-*O*-L-Rha*f*-β-D-Gal*f*; R³ = H
(5) R¹ = β-L-Rha*f*; R² = 6-*O*-β-L-Rha*f*-β-D-Gal*f*; R³ = H
(6) R¹ = α-L-Rha*p*; R² = R³ = H
(7) R¹ = R² = H; R³ = CH₂Ph
(8) R¹ = α-L-Rha*p*; R² = H; R³ = CH₂Ph
(9) R¹ = R³ = H; R² = 6-*O*-α-L-Rha*p*-β-D-Gal*p*
(10) R¹ = R³ = CH₂Ph; R² = H
(11) R¹ = R³ = CH₂Ph; R² = 6-*O*-α-L-Rha*p*-β-D-Gal*p*
(12) R¹ = α-L-Rha*p*; R² = 6-*O*-α-L-Rha*p*-β-D-Gal*p*; R³ = CH₂Ph

Litvinenko and Makarov reported [31] that treatment of robinin with boiling 0·5% aqueous KOH gave rise to a kaempferol-3-*O*-rhamnosido-galactoside, which was found later to be identical with biorobin, a substance isolated from the unripe fruits of *Robinia pseudoacacia* [32]. It was claimed [5,7,8,32] that the glycosyl moiety of biorobin was not β-robinobiosyl but 6-*O*-β-L-rhamnofuranosyl-β-D-galactofuranosyl. Alkaline hydrolysis of our sample of robinin under the conditions specified [31] gave rise to a product which was identical in every respect (mp; $[\alpha]_D$, IR and UV) with biorobin. Total methylation of this material gave again only such alditol acetates (2,3,4-tri-*O*-methylrhamnitol diacetate and 2,3,4-tri-*O*-methylgalactitol diacetate) which were compatible only with the presence of pyranoside and not furanoside hexoses.

The configuration of the glycosidic linkages has been determined by the synthesis of kaempferol-3-*O*-(6-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside) (**9**). For this purpose kaempferol-7,4′-dibenzyl ether [26] (**10**) was coupled with hexa-*O*-acetyl-(6-*O*-α-L-rhamnopyranosyl-α-D-galactopyranosyl)bromide (α-acetobromorobinobiose) to yield after saponification **11**. This was debenzylated by catalytic hydrogenation to **9**, that was identical in every respect with the kaempferol-3-*O*-rhamnosidogalactoside obtained by partial alkaline hydrolysis of robinin. α-Acetobromorobinobiose was prepared from robinobiose heptaacetate which was in turn synthesised using a modification of the method of Kamiya [33]. The configuration of the rhamnose unit follows from the synthetic route leading to the parent robinobiose heptaacetate. This was analogous to that used for the preparation of hepta-*O*-acetyl-6-*O*-α-L-rhamnopyranosyl-β-D-glucopyranoside (β-rutinoseheptaacetate) [33] in which the α-configuration of rhamnose has been unambiguously established by Gorin and Perlin [18]. Also it is known [34], that 1,2-*cis*-peracetyl-glycopyranosyl halides react with anionic aglycones such as phenols in the presence of silver salts in pyridine or quinoline to yield 1,2-*trans*-glycosides, i.e. the robinobiose-kaempferol linkage should be of β-configuration.

These experiments demonstrate that the disaccharide moiety of both robinin and biorobin is robinobiose (6-*O*-α-L-rhamnopyranosyl-D-galactose) attached to the aglycone with a β-pyranosyl linkage and also represent the first synthesis of biorobin.

Since the yield of kaempferol-7-*O*-α-rhamnopyranoside (**6**) obtained by partial acidic hydrolysis of robinin was only 25% and so the possibility that the isomeric rhamnosides described by Maksjutin *et al.* had been lost during the isolation procedure could not be ruled out completely, we carried out the methylation analysis of intact robinin too. This also failed to produce any alditol acetates which could have indicated the presence of hexofuranoside units.

A final proof that robinin was a homogeneous substance having structure **1** was provided by its total synthesis. For this the 4′-benzyl ether of kaempferol-7-*O*-α-L-rhamnopyranoside (**8**) served as key intermediate. Coupling of this with α-acetobromorobinobiose gave after saponification the 4′-benzyl ether of robinin (**12**). Debenzylation of **12** gave kaempferol-3-*O*-(6-α-L-rhamnopyranosyl-β-D-galactopyranoside)-7-*O*-α-L-rhamnopyranoside (**1**), identical in every respect with a sample of natural robinin. It has to be noted that the IR spectra of both are superimposable with that of a specimen isolated from *Robinia viscosa* and reproduced in ref. [5].

Our findings not only confirm Zemplén's structure of robinin but also challenge the structure of numerous other flavonoid glycosides for which the presence of hexofuranoside moieties has been postulated based solely on IR spectra and molecular rotation values (for list, see ref. [35]). Harborne and Robins [see 35] have recently found that a reputed quercetin 3-rhamnofuranoside from *Aesculus* [36] is, in fact, the well known 3-rhamnopyranoside, quercitrin.

EXPERIMENTAL

Mp's were taken on a Kofler microhotstage and are uncorrected. IR spectra were recorded on KBr pellets, NMR spectra at 100 MHz for ^{1}H and 23·5 MHz for ^{13}C with TMS as internal standard. Chromatographic separations were made on Si gel with EtOAc-MeOH-H_2O (200:33:27) as eluant. Acetylations were carried out by Py-Ac_2O at room temp. for 48 hr.

Partial hydrolysis of natural robinin. (a) *Acidic hydrolysis.* Robinin (800 mg) was boiled for 2 hr in 0·16% aq HCl (140 ml) and MeOH (60 ml). After evaporation of the MeOH *in vacuo* the aq soln was extracted with EtOAc (3 × 10 ml). The extract was washed with H_2O, dried, evaporated and chromatographed to give after fractionation [illegible] kaempferol-7-O-α-L-rhamnopyranoside (**6**) [illegible] from 80%

aq MeOH), mp 229–231° (lit. 226–228°, [23] 221–222° [24], 230° [14]; (Found: C, 58·00; H, 4·49. Calc. for $C_{21}H_{20}O_{10}$: C, 58·33; H, 4·66%); UV (EtOH): 225, 255 and 360 nm. $[\alpha]_D$ = −130° (*c* = 0·2, MeOH).

(b) *Alkaline hydrolysis.* Robinin (750 mg) was heated on a steam bath in 0·5% aq KOH (350 ml) for 2 hr. After neutralisation with AcOH the soln was evaporated *in vacuo* and the residue chromatographed in order to separate from unhydrolysed robinin. *Kaempferol-3-O-β-*robinobioside (**9**) (200 mg, 33%, from 10% aq Me_2CO) was eluted first. Mp 223–225° (sintering at 197°), (lit. mp for biorobin [32] 221–223°). (Found: C, 52·47; H, 5·32; H_2O, 2·91. Calc. for $C_{27}H_{30}O_{15}$. H_2O: C, 52·81, H, 5·27; H_2O, 2·91%); $[\alpha]_D$ = −75° (*c* = 1·0, pyridine) [lit. [32] −75° (*c* = 1·0 pyridine)].

Permethylation of natural robinin and its hydrolysis products and preparation of alditol acetates. The glycoside (**1**, **6** or **9**) (5 mg) was dissolved in dry DMSO (5 ml), a suspension of NaH in petrol (50 mg) added and the mixture sealed in N_2 in a vial provided with a rubber septum. After 3 hr shaking at 40° in an ultrasonic mixer, MeI (1 ml) was injected at 0° and the mixture left standing at room temp. for 24 hr. After the addition of 10% aq EtOH the solution was extracted with $CHCl_3$, the organic layer dried and evaporated. The residue was hydrolysed with 2N H_2SO_4 at 100° for 20 hr, neutralised with $BaCO_3$ and filtered. $NaBH_4$ (50 mg) was added and after 3 hr the soln was neutralised with Dowex 50 and evaporated. MeOH was added and evaporated several times to remove boric acid. The residue was acetylated with Py–Ac_2O on the steam bath for 2 hr, the reagent evaporated. The residue was examined by GC–MS.

Characterisation of the alditol acetates. GC–MS analyses were conducted on a column of OV-225 S.C.O.T. (15 m × 0·5 mm) (Perkin-Elmer). The alditol acetate derived from kaempferol-7-*O*-rhamnoside (**6**) gave one major peak on GLC identified as a 2,3,4-tri-*O*-methyl-6-deoxyhexitol diacetate. MS: *m/e* (rel. int.) 175 (9,7), 161 (21), 131 (78), 117 (69), 115 (49), 101 (100), 89 (60), 88 (11), 87 (19), 84 (13), 73 (11), 72 (27), 71 (11), 58 (14), 45 (23), 43 (52), 38 (21), 36 (58) and 35 (10). On GLC of the alditol acetates derived from kaempferol-3-*O*-rhamnosidogalactoside (**7**) first 2,3,4-tri-*O*-methylrhamnitol diacetate was eluted, than a 2,3,4-tri-*O*-methylhexitol triacetate. MS: *m/e* (rel. int.) 230 (37), 189 (47), 173 (25), 161 (45), 159 (28), 129 (98), 117 (100), 113 (21), 101 (97), 99 (97), 89 (11), 88 (24), 87 (89), 85 (10), 74 (13), 73 (11), 72 (13), 70 (33), 68 (10), 59 (11), 58 (16), 45 (30), 44 (87), 43 (98), 41 (10) and 40 (18). GC–MS examination of the alditol acetates prepared from robinin (**1**) did not indicate the presence of compounds different from those described above.

*4′-Benzyloxy-3,5,7-trihydroxyflavone-7-O-α-*L*-rhamnopyranoside* (**8**). To a soln of **7** (2·1 g) [27] in quinoline (25 ml), Drierite (3·0 g), Ag_2O (1·4 g) and 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide [26] (3·0 g) was added at 0°. After stirring for 1·5 hr in the dark another portion (1·0 g) of the bromide was added and stirring continued for another 1·5 hr. The mixture was filtered into chilled 3% aq H_2SO_4 (450 ml), the ppt separated, dried and dissolved in MeOH–Me_2CO (1:1) (30 ml). The soln was adjusted to pH 10 with 1N NaOMe and left to stay overnight. After evaporation, acidification with 5% aq HCl, extraction with EtOAc and repeated evaporation the residue was chromatographed. After fractions of the unchanged aglycone (1·5 g), the rhamnoside (100 mg, 3·5%) was collected. Yellow needles (from MeOH), mp 249–252°. (Found: C, 64·82; H, 5·46. $C_{28}H_{26}O_{10}$ requires: C, 64·36; H, 5·02%). *Pentaacetate.* Colorless amorphous powder (from EtOH–Me_2CO 9:1), mp 132–135°. (Found: C, 61·85, H, 5·23. $C_{38}H_{36}O_{15}$ requires: C, 62·29; 4·95%).

*5,7,3′,4′-Tetrahydroxyflavone-7-O-α-*L*-rhamnopyranoside, Kaempferol-7-O-α-*L*-rhamnopyranoside* (**6**).

A soln of **8** (100 mg) in EtOH (10 ml) was hydrogenated over Pd/C to afford **6** (60 mg 70%) mp 229–231° (from aq EtOH) undepressed on admixture with **6** obtained from natural robinin. IR and UV spectra of both sample were superimposable; $[\alpha]_D^{20}$ = −128° (*c* = 0·25, MeOH). *Hexaacetate.* Colorless flakes, mp 130–132° (from MeOH–Me_2CO 9:1); (Found: C, 57·48; H, 4·89. $C_{33}H_{32}O_{16}$ requires: C, 57·89; H, 4·7%); ^{1}H-NMR: Aglycon (in $CDCl_3$) δ = 2·31, 2·33 and 2·43 (3H each, *s*, 3xOAc), 6·82 (1H, *d*, $J_{6,8}$ 2·0 Hz, C-6), 6·13 (1H, *d*, *J* 2·0 Hz, C-8), 7·26 (2H, *d*, J_0 8·5 Hz, C-3′,5′), 7·86 (2H, *d*, J_0 8·5 Hz, C-2′,6′); Rhamnose (in C_6D_6): δ = 1·23 (3H, *d*, $J_{5,6}$ 6·0 Hz, Me), 2·03, 2·06 and 2·31 (3H each, *s*, OAc), 3·90 (1H, *d*, $J_{5,6}$ 6·0, C-5), 5·26 (1H, *d*, $J_{1,2}$ 2·0, C-1), 5·47 (1H, *t*, $J_{3,4}$ $J_{4,5}$ 9·5 Hz, C-4), 5·65 (1H, *q*, $J_{1,2}$ 2·0, $J_{2,3}$ 3·0 Hz, C-2), and 5·77 (1H, *q*, $J_{2,3}$ 3·0, $J_{3,4}$ 9·5 Hz, C-3) ppm. On irradiation at 3·9 and 5·3 ppm resp. the C-4 triplet and the C-2 quartet resp. collapsed to doublets ($J_{3,4}$ 9·4 and $J_{2,3}$ 3·0 Hz).

*7,4′-Dibenzyloxy-3,5-dihydroxyflavone-3-*O*-(6-O-α-*L*-rhamnopyranosyl-β-*D*-galactopyranoside)* (**11**). Coupling of **10** [26] (0·6 g) in quinoline (40 ml) with hexa-*O*-acetyl-6-*O*-α-L-rhamnopyranosyl-α-D-galactopyranosyl bromide (1·3 g) in the presence of Ag_2O (0·3 g) and Drierite (1·0 g) as described for **8** yielded after saponification with NaOMe, acidification with Amberlite IR 120 resin, evaporation and trituration with acetone chromatographically pure **11** (0·31 g, 31%). Recrystallisation from 60% aq MeOH gave pale yellow platelets of mp 156–158°. (Found: C, 61·85; H, 5·59. $C_{41}H_{42}O_{15}$. H_2O requires: C, 61·97; H, 6·10%).

*3,5,7,4′-Tetrahydroxyflavone-3-*O*-(6-O-α-*L*-rhamnopyranosyl-β-*D*-galactopyranoside); Kaempferol-3-O-β-robinobioside, Biorobin* (**9**). **11** (150 mg) was debenzylated by catalytic hydrogenation in EtOH to yield **9** (100 mg, 87%) as yellow needles (from 10% aq Me_2CO) of mp 224–226° (sintering at 198°) undepressed on admixture with a sample obtained by alkaline hydrolysis of robinin. $[\alpha]_D^{20}$ = −75° (*c* = 1·0, pyridine), biorobin [32] mp 221–223°, $[\alpha_D]$ = −75 (*c* = 1·0, pyridin). IR spectra of the 2 samples were superimposable. *Nonaacetate.* Colorless amorphous powder (from EtOH–$CHCl_3$ 9:1), mp 136–139°.

*4-Benzyloxy-3,5,7-trihydroxyflavone 7-*O*-α-*L*-rhamnopyranoside-3-*O*-(6-O-α-*L*-rhamnopyranosyl-β-*D*-galactopyranoside)* (**12**). Coupling of **8** (0·34 g) with hexa-*O*-acetyl-6-*O*-α-L-rhamnopyranosyl-α-D-galactopyranosyl bromide (1·0 g) as described for **11** gave after saponification and chromatographic separation from unreacted **8** chromatographically pure **12** (110 mg, 21%), yellow needles of mp 254–256° (from 90% EtOH); (Found: C, 58·08; H, 5·32; $C_{40}H_{46}O_{19}$ requires: C, 57,83; H, 5·58%).

*3,5,7,4′-Tetrahydroxyflavone-7-*O*-α-*L*-rhamnopyranoside-3-*O*-(6-O-α-*L*-rhamnopyranosyl-β-*D*-galactopyranoside); robinin* (**1**). **12** (150 mg) was debenzylated by catalytic hydrogenation in EtOH. The filtered solution was evaporated and the residue triturated with Me_2CO to give **1** (100 mg, 78%) as a yellow powder of mp 250–254°. Recrystallization from 50% aq MeOH afforded the hydrate as yellow needles of mp 196–199° undepressed on admixture of natural robinin. $[\alpha]_D^{20}$ = −103° (*c* = 1·0, pyridin) (lit. [1] mp 195–197°; lit. [7] $[\alpha]_D^{20}$ − 122–5° (*c* = 1, H_2O–pyridine 1 : 1)); (Found: C, 51·88; H, 5·40; H_2O, 2·50; $C_{33}H_{40}O_{19}$. H_2O requires: C, 51–11; H, 5·58; H_2O, 2·37%). IR spectra of the 2 samples were superimposable. *Undecaacetate.* Amorphous powder (from EtOH–$CHCl_3$ 15 : 1), mp 142–145°C, (Found: C, 54–73; H, 5·17. Calc. for. $C_{45}H_{48}O_{24}$: C 55·55; H, 4·97%).

Acknowledgements—We are indebted to Prof. B. Lindberg, Dr. L. Kenne (Stockholm), and Dr. M. Mészáros for assistance in the methylation analysis, further to Dr. L. Radics, Mrs. M. Kajtár and Mrs. E. Gács for NMR-spectra.

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