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DISTRIBUTION OF FLAVONOIDS IN THE GENUS *BAPTISIA* (LEGUMINOSAE)

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Abstract—Distributional data for sixty-two flavonoids and two coumarins in all 17 spp. of the genus *Baptisia* are presented.

INTRODUCTION AND DISCUSSION

PLANT spp. in the genus *Baptisia* are rich in flavonoids and much use has been made of flavonoid distributional data in this genus for the purposes of species recognition,[1-4] hybrid analysis[3,5-10] and detection of introgression.[3,7] As a result, numerous scattered articles on the flavonoid chemistry of individual *Baptisia* species have appeared in the literature over the past 10 yr.[1,3,4,10-14] It was therefore considered worthwhile to compile these data and to extend them to include all previously uninvestigated species in the hope that a survey of the whole genus would provide further information on relationships within the genus.

Distributional data for some 62 of the major flavonoids and two coumarins in all 17 spp. of genus *Baptisia* are presented in Tables 1 and 2.† Every flavonoid listed was isolated and characterized from at least one *Baptisia* spp.,‡ the majority from *B. lecontei*,[1,11,13] *B. australis*,[4,12] *B. sphaerocarpa*,[10,14] *B. leucantha*[10] and *B. alba*.[10] The presence or absence of previously encountered *Baptisia* flavonoids in species other than these was established by means of paper chromatography, hydrolysis and u.v. spectroscopy, while entirely new compounds detected in the survey (e.g. texasin,[12] calycosin[11] and 6-hydroxygenistein)[11] were isolated and fully characterized.

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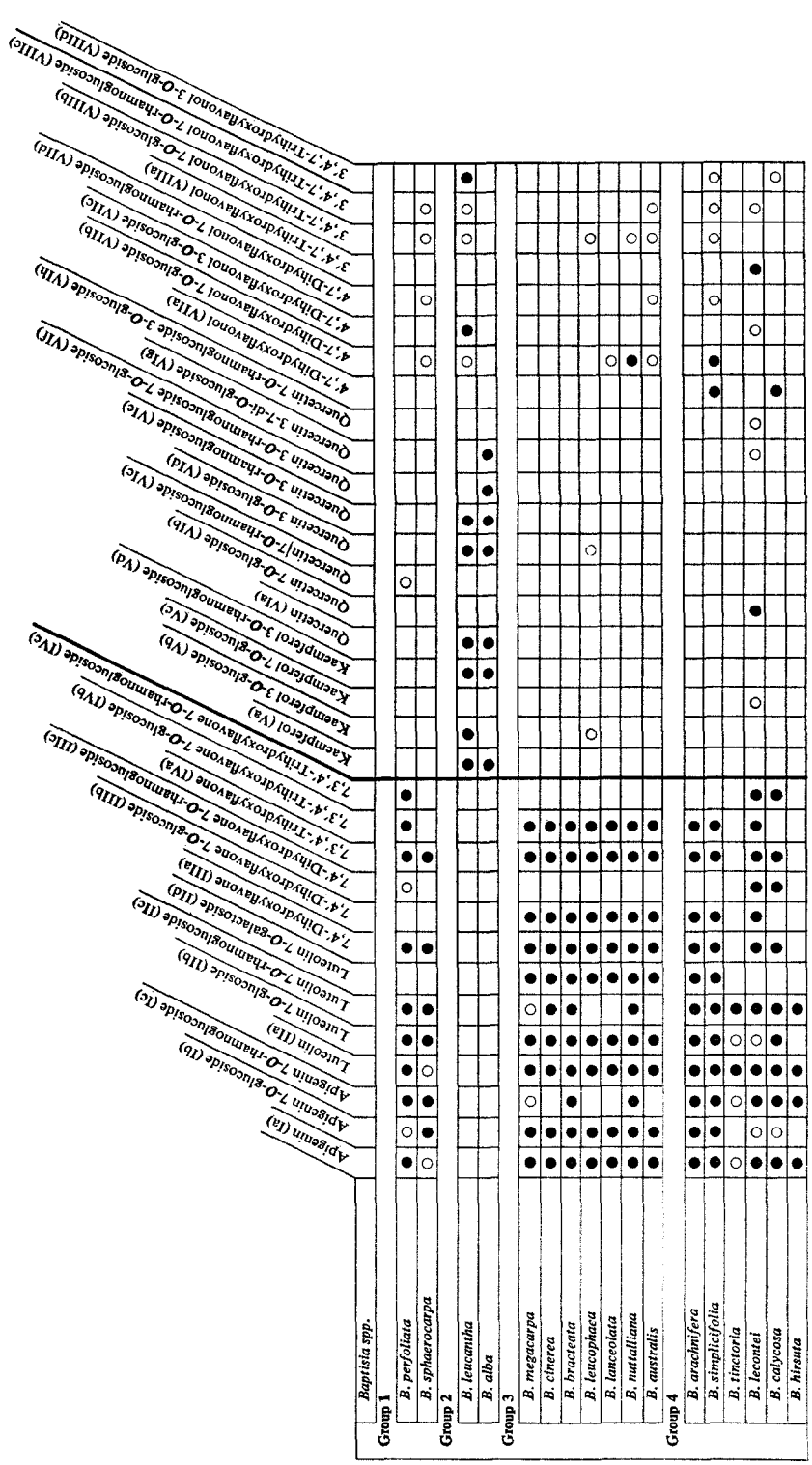
† The alignment of the *Baptisia* spp. into groups 1, 2, 3, and 4 in Tables 1 and 2 is based upon both morphological and chemical information.

‡ Although some of the aglycones reported in Tables 1 and 2 may have arisen by glycosidic breakdown during the drying of the plant material or during the work-up procedures, most (if not all) were also encountered when fresh plant material was employed for extraction purposes.

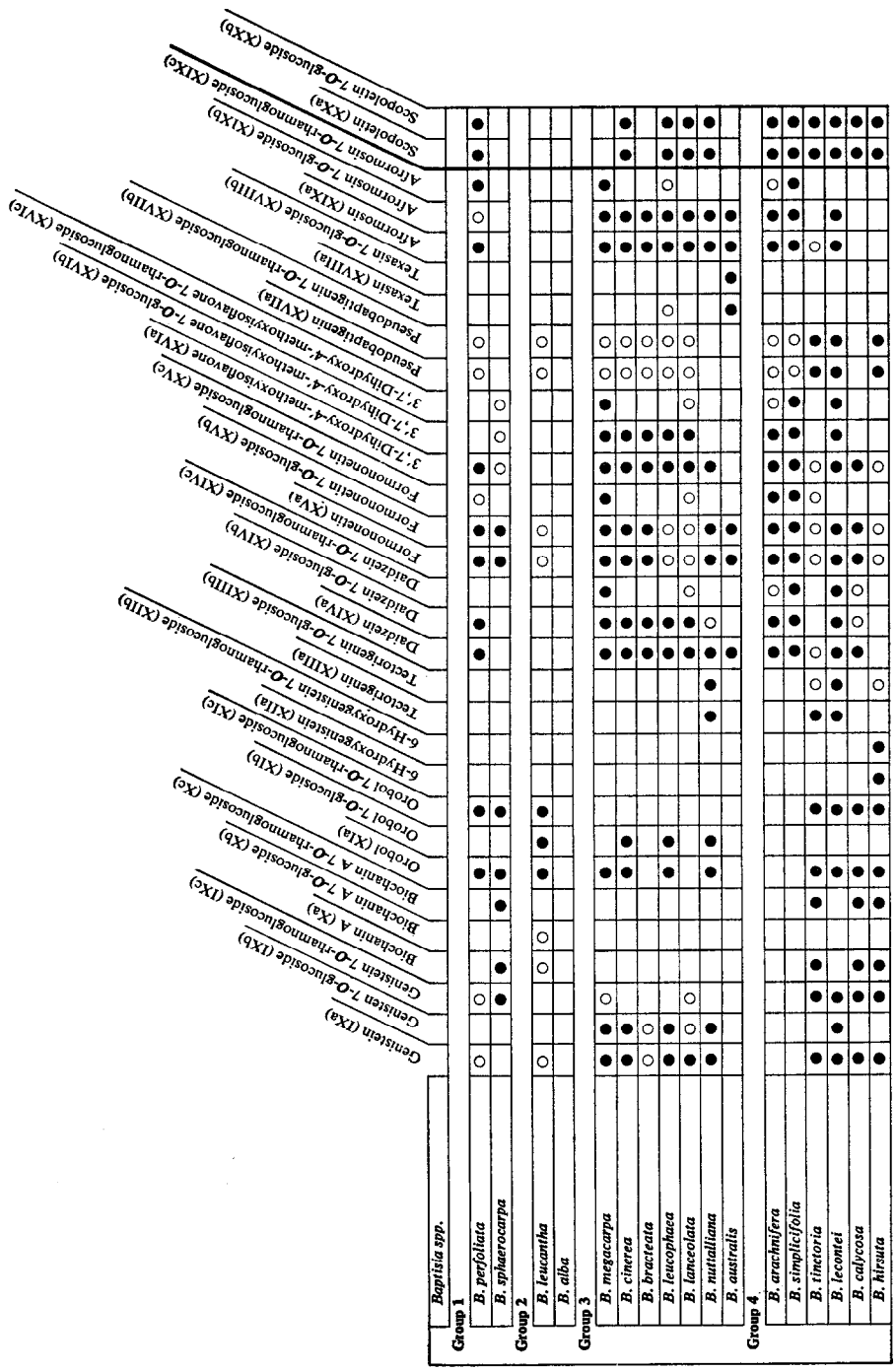
[1] K. R. MARKHAM and T. J. MABRY, *Phytochem.* **7**, 791 (1968).
[2] B. G. BREHM and R. E. ALSTON, *Am. J. Botany* **51**, 644 (1964).
[3] B. L. TURNER, *Pure Appl. Chem.* **14**, 189 (1967).
[4] P. LEBRETON, K. R. MARKHAM, W. T. SWIFT, OUNG-BORAN and T. J. MABRY, *Phytochem.* **6**, 1675 (1967).
[5] R. E. ALSTON, *Taxon* **14**, 268 (1965).
[6] R. E. ALSTON and K. HEMPEL, *J. Heredity* **55**, 267 (1964).
[7] R. E. ALSTON and B. L. TURNER, *Am. J. Botany* **50**, 159 (1963).
[8] R. E. ALSTON and B. L. TURNER, *Proc. Natl. Acad. Sci. U.S.* **48**, 130 (1962).
[9] R. E. ALSTON, B. L. TURNER, R. N. LESTER and D. HORNE, *Science* **137**, 1048 (1962).
[10] R. E. ALSTON, H. RÖSLER, K. NAIFEH and T. J. MABRY, *Proc. Natl. Acad. Sci. U.S.* **54**, 1458 (1965).
[11] K. R. MARKHAM, T. J. MABRY and W. T. SWIFT, *Phytochem.* **7**, 803 (1968).
[12] K. R. MARKHAM, W. T. SWIFT and T. J. MABRY, *J. Org. Chem.* **33**, 462 (1968).
[13] K. R. MARKHAM and T. J. MABRY, *Tetrahedron* **24**, 823 (1968).
[14] H. RÖSLER, T. J. MABRY and J. KAGAN, *Chem. Ber.* **98**, 2193 (1965).

TABLE 1. DISTRIBUTION OF FLAVONES AND FLAVONOLS IN *Baptisia*



● = Major; ○ = trace.

TABLE 2. DISTRIBUTION OF *iso*FLAVONES AND COUMARINS IN *Baptisia*



Although we hope to publish a full botanically oriented analysis of these results at a later date, one significant point does emerge from this survey and that is the chemical similarity of *B. megacarpa* with the species of group 3. Prior to this survey *B. megacarpa* had been grouped with the white-flowered species *B. alba* and *B. leucantha* in group 2, mainly on the basis of its fruit and vegetative features.[3] However, floral characters favor an alliance with the *B. leucophaea* group[3] and the chemical data presented in Table 1 lend strong support to this. Accordingly we have placed *B. megacarpa* in group 3.

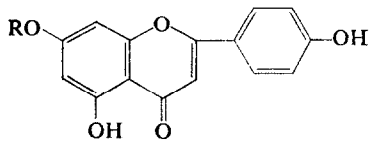
EXPERIMENTAL

Origin of Plant Material

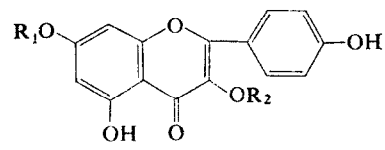
For the origin of plant material from the *Baptisia* spp. *lecontei, australis* and *hirsuta*[1,11] and for all the other species, the collection sites were the same or nearly the same as those reported previously.[15] Most of the plant material used in the present survey was collected in late May 1967.*

Method of Analysis for Spp. not Thoroughly Investigated Previously

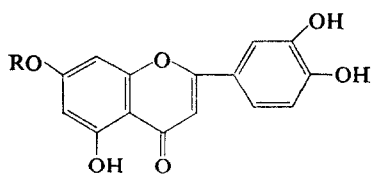
A 5 g sample of dry plant material consisting of leaves and stems was pulverized in a Waring blendor and then extracted for several days at 20° with aq. methanol (1:4) (30–40 ml). The extract was removed by filtration and a portion of it chromatographed in two dimensions on Whatman 3MM paper using as solvents: (1) *t*-BuOH–HOAc–H_2O (3:1:1) and (2) 15% HOAc. The resultant chromatogram was viewed in u.v. light (360 nm) alone, and in the presence of ammonia vapor.



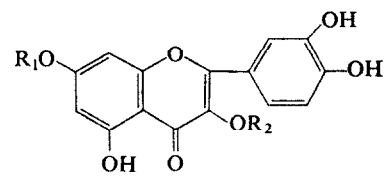
(Ia) R = H
(Ib) R = glucosyl
(Ic) R = rhamnoglucosyl



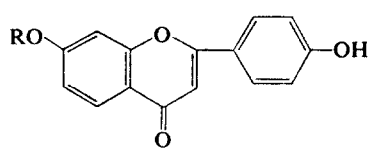
(Va) R_1,R_2 = H
(Vb) R_1 = H; R_2 = glucosyl
(Vc) R_1 = glucosyl; R_2 = H
(Vd) R_1 = H: R_2 = rhamnoglucosyl



(IIa) R = H
(IIb) R = glucosyl
(IIc) R = rhamnoglucosyl
(IId) R = galactosyl



(VIa) R_1,R_2 = H
(VIb) R_1 = glucosyl; R_2 = H
(VIc) R_1 = rhamnoglucosyl; R_2 = H
(VId) R_1 = H; R_2 = glucosyl
(VIe) R_1 = H; R_2 = rhamnoglucosyl
(VIf) R_1 = glucosyl; R_2 = rhamnoglucosyl
(VIg) R_1,R_2 = glucosyl
(VIh) R_1 = rhamnoglucosyl; R_2 = glucosyl



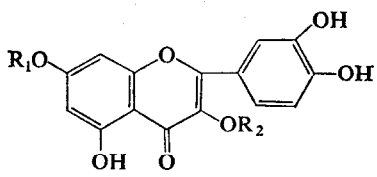
(IIIa) R = H
(IIIb) R = glucosyl
(IIIc) R = rhamnoglucosyl

SCHEME 1.

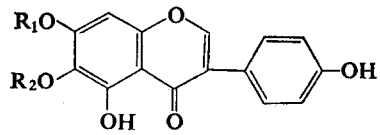
* Numerous vouchers from the May 1967 collection trip as well as earlier ones are deposited in the Herbarium, The University of Texas at Austin, Austin, Texas, U.S.A.

[15] M. F. CRANMER and T. J. MABRY, *Phytochem.* **5**, 1133 (1966).

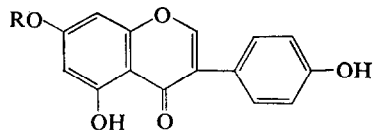
The chromatographic patterns obtained for the newly investigated *Baptisia* spp. (*perfoliata, megacarpa, cinerea, bracteata, lanceolata, nuttalliana, arachnifera, tinctoria, calycosa, hirsuta, simplicifolia* and *leucophaea*) were compared directly with the patterns of spp. whose chemistry had been investigated more thoroughly, e.g. *lecontei, sphaerocarpa, leucantha, alba* and *australis*. By this means it was possible to establish the presence or absence of a wide range of flavonoids for which structures had previously been established. In cases where there was doubt about the identification, the spot in question was cut from the chromatogram and the compound which was eluted from it was compared chromatographically and spectrally with the authentic flavonoid isolated from a species in which it was known to occur. Acid hydrolyses were frequently carried out to establish the aglycone, and in such cases the sugars released were analysed by the method of Pridham.[16]



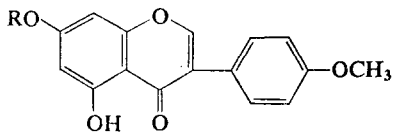
(VIIIa) R_1,R_2 = H
(VIIIb) R_1 = glucosyl; R_2 = H
(VIIIc) R_1 = rhamnoglucosyl; R_2 = H
(VIIId) R_1 = H; R_2 = glucosyl



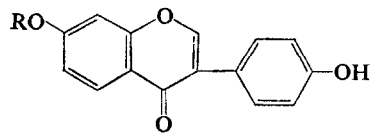
(XIIa) R_1,R_2 = H
(XIIb) R_1 = rhamnoglucosyl; R_2 = H
(XIIIa) R_1 = H; R_2 = CH_3
(XIIIb) R_1 = glucosyl; R_2 = CH_3



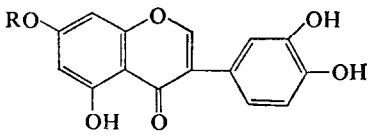
(IXa) R = H
(IXb) R = glucosyl
(IXc) R = rhamnoglucosyl



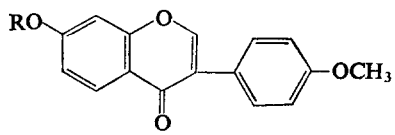
(Xa) R = H
(Xb) R = glucosyl
(Xc) R = rhamnoglucosyl



(XIVa) R = H
(XIVb) R = glucosyl
(XIVc) R = rhamnoglucosyl



(XIa) R = H
(XIb) R = glucosyl
(XIc) R = rhamnoglucosyl



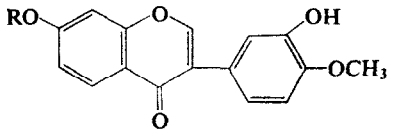
(XVa) R = H
(XVb) R = glucosyl
(XVc) R = rhamnoglucosyl

SCHEME 2.

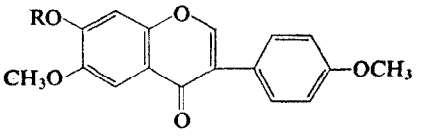
In order to determine which isoflavone aglycones were present, it was usually necessary to cut the whole isoflavone aglycone region[17] from the initial 2D chromatogram and rechromatograph the eluted isoflavones in a solvent consisting of the benzene layer of a mixture of benzene–HOAc–H_2O (6:7:3).

[16] J. B. PRIDHAM, *Anal. Chem.* **28**, 1967 (1956).
[17] T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer-Verlag, New York (1970).

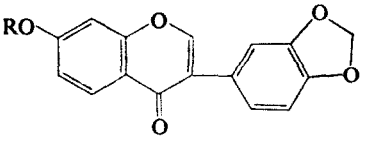
When entirely new compounds were detected these were isolated in quantity and an attempt was made to characterize them. Much of this work has been published elsewhere (e.g. Refs. 11, 12 and 13).



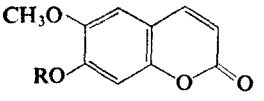
(XVIa) R = H
(XVIb) R = glucosyl
(XVIc) R = rhamnoglucosyl



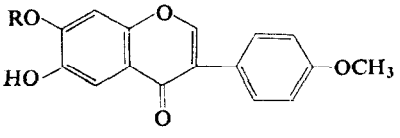
(XIXa) R = H
(XIXb) R = glucosyl
(XIXc) R = rhamnoglucosyl



(XVIIa) R = H
(XVIIb) R = rhamnoglucosyl



(XXa) R = H
(XXb) R = glucosyl



(XVIIIa) R = H
(XVIIIb) R = glucosyl

SCHEME 3.

The presence or absence of the coumarin, scopoletin, and its glucoside, in all species but *B. lecontei*, was established on the basis of paper chromatography alone.

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