eluate on repeated preparative-TLC purification using C_6H_6–EtOAc (1:1) gave three 2-methylisoflavones [2] and another fraction now identified as a new 2-methylisoflavone, glyzarin.

Glyzarin (50 mg), light yellow needles from EtOH, mp 207–8°, $C_{18}H_{14}O_4$ (M^+ 294; Found: C, 73.7; H, 4.3; required C, 73.4; H, 4.7%). It gave −ve Mg–HCl, −ve Zn–HCl but +ve Na–Hg/HCl tests and had λ_{max}^{MeOH} (log ε) 250 (4.13), 295 (3.74); +NaOAc 273, 317 nm; ν_{max}^{KBr} 3450, 1740, 1680 cm^{-1}. The colour reactions and UV spectrum indicated the possibility of glyzarin being an isoflavone. MS: *m/e* (rel. intensity) 294 (M^+) (100), 252 (98), 137 (33), 136 (28), 116 (55), and 77 (58). It gave an acetate (Ac_2O–Py) as colourless needles from aq. EtOH, mp 198–9°. PMR spectrum of glyzarin acetate (δ, $CDCl_3$; TMS internal standard): 2.35, 2.40 (6H, *s*, –OCOMe, C–Me), 3.00 (3H, *s*, –COMe), 7.20 (1H, *d*, *Jo* = 8 Hz, 6-H), 7.55 (5H, *m*, side phenyl protons), 8.10 (1H, *d*, *Jo* = 8Hz, 5-H). The spectral data showed C–Me, C–acetyl and O–acetyl substituents and an unsubstituted side phenyl ring. The latter was also confirmed by the identification of phenylacetic acid after alkaline hydrolysis of glyzarin and its UV spectrum showed bathochromic shifts with NaOAc characteristic of a C-7 OH [4]. In addition a brown ferric reaction indicated the possibility of this OH being chelated with C-acetyl which could be thus considered at C-6 or C-7. In the PMR the signals at δ7.20 and 8.10 were assigned to the two *ortho*-coupled aromatic protons present at C-6 and C-5 respectively and the C-acetyl was thus placed at C-8. Since the signal due to the H at C-2 in isoflavones in the region of δ 7.60–7.88 [4] was absent, the remaining C–Me was fixed at C-2. Thus glyzarin was assigned the structure 2-methyl-7-hydroxy-8-acetylisoflavone which was confirmed by comparison with a synthetic sample obtained by heating 2-methyl-7-acetoxyisoflavone [6] with $AlCl_3$ under the conditions of Fries migration (mp, mmp, Co–TLC and superimposable IR).

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ISOLATION AND CONSTITUTION OF CORYLIDIN: A NEW COUMESTROL FROM THE FRUITS OF *PSORALEA CORYLIFOLIA*

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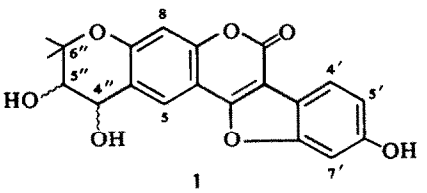
Key Word Index—*Psoralea corylifolia*; Leguminosae; triacontane; sitosterol-D-glucoside; 4″,5″-*cis*-dihydroxyisosporalidin.

Previous work has been reported on the fruits of *Psoralea corylifolia* [1–4], and related species *P. drupaceae* [5–10], *P. plicata* [11] and *P. acaulis* [12].

The ether extract (800 g) of the whole dried seeds of *P. corylifolia* (5 g) was separated into individual constituents by repeated column chromatography over Si gel.

Elution with petrol (40–60°) afforded triacontane $C_{30}H_{62}$ mp 63–4°, mmp undepressed, TLC and Co-TLC, identical in all respects with the authentic sample.

The C_6H_6–Et_2O (1:3) eluate yielded corylidin (1) as white crystalline needles (from EtOH–Me_2CO) (60 mg), mp 349–51°. It gives no ferric chloride reaction but a yellow colouration was obtained with aq. NaOH. The compound analysed for $C_{20}H_{16}O_7$, M^+ 368.0867 ($C_{20}H_{16}O_7$ req. M^+ 368.0894) λ_{max}^{EtOH} nm (log ε) 210 (4.61), 220 (*sh* 4.38), 245 (4.26), 298 (*sh* 4.08), 312 (3.92), (4.40) and 365 (*sh* 4.35) which remained unaffected on the addition of NaOAc or $AlCl_3$, but shifted to λ_{max} 275 nm on the addition of ethanolic KOH. IR ν_{max}^{KBr} cm^{-1}: 3360, 3210, 3100, 2980, 1701, 1635, 1610; 1575, 1495, 1450, and 870. NMR (100 MHz, d_6-DMSO): two sharp singlets at δ1.13 and 1.17 (3H each, $(Me)_2C<$), a one proton doublet at 4.27 ($J_{5'',4''}$ = 4.5 Hz, C-5″ proton). There was a broad signal at 5.29 due to the C-4″ proton which changed to a sharp doublet ($J_{4'',5''}$ = 4·5 Hz) on D_2O exchange, a double doublet at 6.89 (J = 8.1 and 2.1 Hz, 1H; C-5′), a singlet at 6.99 (1H, C-8), a doublet at 7.12 (J = 2.1 Hz, 1H C-7′), a proton doublet at 7.65 (J = 8.1 Hz, 1H C-4′) and a singlet at 7.86 (1H, C-5).



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The MS showed prominent peaks at *m/e* (rel. int.) 368 (M^+, 100%), (24.4), 355 (96.51), (75.6), 308 (24.4), 296 (98.8), 293 (98.8), 292 (95.3), 281 (12.8), 69 (43.2), 59 (100) 43 (100), which was consistent with the structure proposed. The $CHCl_3$–MeOH (9:1) eluate afforded

β-sitosterol-D-glucoside, $C_{35}H_{60}O_6$, mp 277–8°, mmp undepressed, Co-TLC and IR, tetra acetate $C_{43}H_{68}O_{10}$, mp 158–9°, mmp Co-TLC and IR, identical in all respects with the authentic sample.

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THE STRUCTURE OF DELPHIDINE, A DITERPENOID ALKALOID FROM *DELPHINIUM STAPHISAGRIA*

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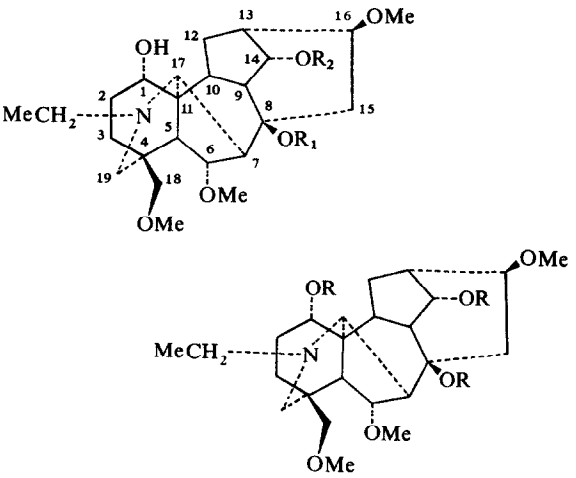
Key Word Index—*Delphinium staphisagria*; Ranunculaceae; C_{19}-diterpenoid alkaloid; Delphidine

We wish to report the structure of delphidine (**1**), a C_{19}-diterpenoid alkaloid isolated from *Delphinium staphisagria*.[1] The mother liquors which had been accumulated during the isolation of delphinine from the seeds of *D. staphisagria* were found to contain a relatively large amorphous fraction of alkaloids [1]. We recently described the isolation, structure, and absolute configuration of a new diterpene alkaloid, delphisine (**2**), from these mother liquors [2]. We report now the isolation of another diterpenoid alkaloid named delphidine (**1**), by a combination of gradient pH extractions and chromatographic techniques.

Delphidine, $C_{26}H_{41}NO_7$ [3], mp 98–100° (with slight softening at 90°), $[\alpha]_D^{27}$ + 16.6° (C ~ 1.3 EtOH) shows broad absorption at 3600 ~ 3000 (H-bonded OH group), 1720 (MeCO group) and 1100 (ether linkage) cm^{-1} in its IR spectrum. The ^1H NMR spectrum shows absorption for an N—$CH_2\underline{CH}_3$ group (3H triplet, J 7 Hz) centred at δ1.13, one acetoxyl group (δ2.00, as 3H singlet) and three OMe groups (3H singlets at δ3.26, δ3.31 and δ3.34). The IR and ^1H NMR spectra of this new alkaloid show some similarity with those of the known alkaloids, delphisine (**2**) and neoline (**3**) [2, 4].

Hydrolysis of delphidine with a solution of K_2CO_3 in aqueous MeOH afforded a triol, $C_{24}H_{39}NO_6$, mp 159–161°, which was identical (IR, ^1H and ^{13}C NMR) with neoline (**3**). Treatment of delphidine with Ac_2O and pyridine at room temperature overnight yielded a compound which proved to be identical with neoline



1 R_1 = —Ac, R_2 = —H
2 R_1 = R_2 = —Ac
3 R = —H
4 R = —Ac

triacetate (**4**) (delphisine 1α-monoacetate), $C_{32}H_{45}NO_9$, mp 149–151°. These results confirm the presence of two free secondary hydroxyl groups in delphidine **1**. The identical triacetate (**4**) (IR, NMR, mp, mmp) was also obtained by the hydrolysis of delphidine to the triol **3**, followed by acetylation of the latter with Ac_2O and *p*-toluenesulfonic acid at 100°.