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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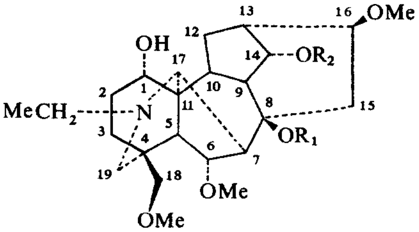

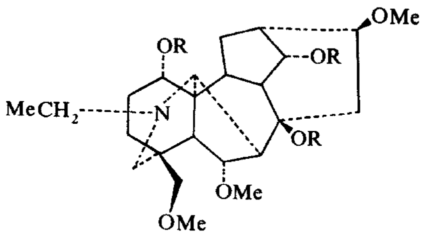

1 R_1 = —Ac, R_2 = —H
2 R_1 = R_2 = —Ac

3 R = —H
4 R = —Ac

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 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°.

On the basis of the above chemical studies, it is clear that the acetyl group in delphidine is present at the C-8 position. We, therefore, assign the structure of 8-acetylneoline (1) to delphidine. Because delphidine (1) has been related to delphisine (2) and neoline (3), the absolute configuration of delphisine derived by an X-ray analysis applies to delphidine as well. It is interesting to note that the C-1 proton signal in delphidine appears as a multiplet at $\delta 3.82$, an observation consistent with ring A in a boat conformation, as in the case of delphisine (2) [2].

When delphisine (2) is allowed to stand in hexane over a column of alumina (Activity III) for three days, and is eluted subsequently with 3% ethanol in hexane, it furnished an almost quantitative yield of delphidine (1). The selective hydrolysis of the 14-acetyl group of delphisine by an alumina column suggests that delphidine (1) might be an artefact formed during chromatographic separation of the alkaloid mixture. We have not been able to rule out this possibility yet [5].

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5. The detailed isolation, chemical studies and ^{13}C NMR analysis on delphidine will be published later along with data on the other alkaloids from *D. staphisagria*.