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BACOGENIN A_2: A NEW SAPOGENIN FROM BACOSIDES*

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Key Word Index—*Bacopa monniera*; Scrophulariaceae; Bacogenin A_2, triterpenoid.

Abstract—By means of physicochemical studies bacogenin A_2 has been shown to be an isomer of bacogenin A_1 differing either in the configuration at C-20 or in the disposition of the vinylic methyl group in the side chain.

THE SAPONINS, bacosides A and B, from *Bacopa monniera* Wettst. furnished a mixture of four aglycones namely bacogenins A_1–A_4 on acid hydrolysis.[1] In the preceding papers the structure of bacogenin A_1[2] and the identification of bacogenin A_4 as ebelin lactone along with the tentative proposals on the nature of the genuine sapogenin have been described.[3] The structure of bacogenin A_2 is reported in the present communication.

Bacogenin A_2, $C_{30}H_{48}O_4$, (M^+ 472) m.p. 220°, contains an OH (3350 cm^{-1}), a 5-membered ring CO (1750 cm^{-1}) and a –C=C–H group (1665, 820 cm^{-1}). Its PMR spectrum exhibited signals for seven tertiary Me, $-CH_2COCH-$, –CHO–, $-CH_2O-$ and Me–C=CH groups. The relative disposition of the vinylic Me and vinylic H as –CH=C–Me was similar to that of bacogenin A_1 and was confirmed by spin decoupling. Further, its PMR spectrum in pyridine d_5 showed, besides other signals, a 2H AB quartet (J 16 Hz) centred at 2·45 ppm and a 1H broad singlet at 2·47 ppm assignable to the methylene and methine protons respectively flanking the C=O group, thereby confirming the existence of a $-CH-CO-CH_2-$ grouping in the 5-membered ring.

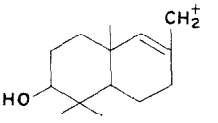
After addition of trichloroacetylisocyanate (TAI), the PMR spectrum of bacogenin A_2 exhibited two 1H broad singlets of –CO–NHCO– protons (8·46 and 8·51 ppm) demonstrating the presence of only two OH groups in the molecule. This was further confirmed by formation of bacogenin A_2 diacetate, $C_{34}H_{52}O_6$, m.p. 202–3°, which showed two acetyl singlets at 2·0 and 2·06 ppm in PMR spectrum. Moreover, the signals due to –CHO– and CH_2–O– now shifted downfield by *ca* 1 and 0·5 ppm respectively suggesting that one of the OH groups was secondary and the other one primary.

The MS of bacogenin A_2 displayed prominent peaks at *m/e* 472 (M^+), 457 (M–15), 439 (M–15–18), 207 (ion *a*) and 189 (207–18). A very intense peak was observed at *m/e* 125 (base peak) due to the side chain (*b*)[2], which on further loss of H_2O and CH_3 gave rise to *m/e* 107 and 110 respectively. The MS of di-*O*-acetylbacogenin A_2 also contained an intense peak at *m/e* 125 suggesting that the side chain of bacogenin A_2 did not carry any OH group.

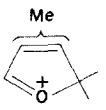
* Part VI in the series "Chemical Examination of *Bacopa monniera*". CDRI communication No. 1865.

[1] CHATTERJI, N., RASTOGI, R. P. and DHAR, M. L. (1965) *Indian J. Chem.* **3**, 24.
[2] KULSHRESHTHA, D. K. and RASTOGI, R. P. (1973) *Phytochemistry* **12**, 887.
[3] KULSHRESHTHA, D. K. and RASTOGI, R. P. (1973) *Phytochemistry* **12**, 2074.

In view of the common molecular formula and functionalities of bacogenin A_1 and A_2 and their similar physicochemical data, bacogenin A_2 was considered to possess a gross structure similar to that of bacogenin A_1 but differing either in the configuration at C-17, C-20 or in the disposition of the vinylic Me group of the side chain.

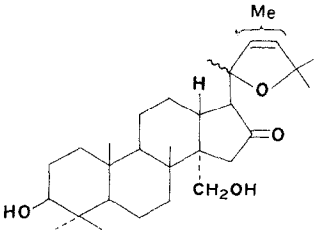


a m/e 207



b m/e 125

In case of the 17 α-configuration, the side chain would be susceptible to base catalysed epimerization because of the activation by the C-16 carbonyl group. Bacogenin A_2 was, however, recovered unchanged on alkali treatment indicating that the side chain possessed 17 β-configuration. Bacogenin A_2 has, therefore, been assigned structure **1**.



(**1**)

EXPERIMENTAL

All m.ps were determined on Kofler block and are uncorrected.

Bacogenin A_2. m.p. 220°, $[\alpha]_D = -44°$ (*c* 1%, EtOH), ν_{max}(KBr): 3350, 2925, 2850, 1750, 1465, 1375, 1200, 1040, 970, 844, 824, 785, 752; *PMR*: ppm 0·80, 0·90, 0·983, 1·25, 1·31 (3H each, *s*, 5 × Me), 1·15 (6H, *s*, 2 × Me), 1·73 (3H, *d*, *J* 1·5 Hz, –C=C–Me), 2·2 (3H, *bs*, –CH–CO–CH_2–), 3·23 (1H, *q*, *J* 10, 5 Hz –CH–O–), 3·966 (2H, ABq, *J* 11 Hz, –CH_2–O–), 5·30 (1H, *q*, *J* 1·5 Hz, –C = C–H); PMR (in pyridine d_5): ppm 0·80, 0·89, 1·15, 1·20, 1·30 (3H each, *s*, 5 × Me), 1·044 (6H, *s*, 2 × Me), 1·69 (3H, *d*, *J* 1·5 Hz, –C=C–Me), 2·45 (1H, *s*, –CH–CO), 2·47 (2H, ABq, *J* 16, CH_2–CO–), 3·29 (1H, *m*, –CH–O), 4·14 (2H, ABq, *J* 12 Hz, –CH_2–O), 5·20 (1H, *q*, *J* 1·5 Hz, –C=C–H). *MS*. *m/e* 472 (M^+), 457, 439, 207, 189, 180, 125 (base peak), 110, 107 (Found: C, 75·98; H, 10·35. $C_{30}H_{48}O_4$ requires: C, 76·27; H, 10·16%).

Di-O-acetylbacogenin A_2. Bacogenin A_2 (500 mg) in pyridine (5 ml) and Ac_2O (5 ml) was allowed to react overnight. The product was crystallised from alcohol, m.p. 202–203°; $[\alpha]_D - 43°$ (*c* 1% $CHCl_3$); PMR: ppm 0·89 (6H, *s*, 2 × Me), 0·95, 1·09, 1·19, 1·25, 1·33 (3H each, *s*, 5 × Me), 1·75 (3H, *d*, *J* 1·5 Hz, –C=C–Me), 2·0, 2·06 (3H each, *s*, OCOMe), 4·48 (2H, ABq, *J* 13 Hz, CH_2OAc), 4·55 (1H, *m*, CHOAc), 5·34 (1H, *q*, *J* 1·5 Hz, C=C–H). MS: *m/e* M^+ (not visible), 542, 449, 481, 457, 439, 421, 397, 189, 125, 107 (Found: C, 73·08; H, 9·86. $C_{34}H_{52}O_6$ requires: C, 73·41; H, 9·606%).

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