Phytochemistry, 1980, Vol. 19, p. 2033. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0901-2033 $02.00/0

THE STRUCTURE OF ACERTANNIN

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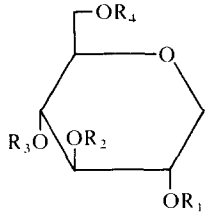
(*Received* 11 *January* 1980)

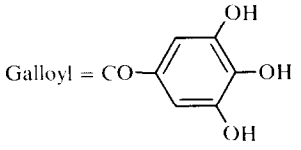
Key Word Index—*Acer ginnala*; Aceraceae; 2,6-di-*O*-galloyl-1,5-anhydro-D-glucitol; acertannin; correction of structure.

Acertannin, first reported as a constituent of *Acer ginnala* Maxim. [1], has been formulated as 3,6-di-*O*-galloyl-1,5-anhydro-D-glucitol (**2**) on the basis of the failure of the aromatic hexa-*O*-methyl derivative to give (a) a positive response to reactions for free primary hydroxy groups, and (b) a vicinal diol-cleavage with periodate [2]. However, on the basis of the spectral properties of acertannin we now conclude that it is 2,6-di-*O*-galloyl-1,5-anhydro-D-glucitol (**3**).

The ^{1}H NMR spectrum of ascertannin has been completely analysed (270 MHz, see Experimental), and the low-field positions of the H-2 and H-6 signals show unequivocally that these must be located at the acylated positions. Furthermore, comparison of the ^{13}C NMR spectrum of **3** with that of **1** gives the assignments for **3** compiled in the Experimental. The downfield shifts of C-2 and C-6, together with the upfield shifts of C-1, C-3 and C-5 for **3** relative to **1**, are likewise in keeping with the former as the acylated positions. The exclusion [2] of **3** as a possible structure for acertannin was based on the fact that the hexamethyl ether failed to react with periodate under a variety of conditions. This could, however, be explained (cf. [4]) by a combination of (a) the *trans*-disposition of the 3- and 4-hydroxy groups, and (b) the presence of galloyl groups in the immediate vicinity of the *vic*-diol.



1 $R_1 = R_2 = R_3 = R_4 = H$
2 $R_1 = R_3 = H$; $R_2 = R_4$ = galloyl
3 $R_2 = R_3 = H$; $R_1 = R_4$ = galloyl



EXPERIMENTAL

Acertannin (**3**) was extracted [2] from dry leaves of *Acer ginnala* Maxim. to give a crystalline product (8%) with mp 162–165° (dec.), $[\alpha]_D^{20}$ + 22° (*c* 0.6; Me_2CO). Lit. [1,2]: mp 164–166°, $[\alpha]_D^{12}$ + 20° (Me_2CO). ^{1}H NMR (270 MHz, CD_3OD); δ 7.26 and 7.25 (6 H, phenolic), 5.06 (*dt*, J = 10, 5.5 Hz, H-2), 4.71 and 4.55 (*d*-like, J = 12 Hz, 2 × H-6), 4.26 (*dd*, J = 11, 5.5 Hz, H-1_{eq}), 3.87 (*t*-like, J = *ca* 9 Hz, H-3), 3.68 (*m*, 2 H, H-4 and H-5), 3.51 (*t*, J = 10.5 Hz, H-1_{ax}); ^{13}C NMR (22.6 MHz, D_2O/DMSO-*d*): δ 168.2 and 167.8 (*s*'s, COO), 146.3 (4 C, *s*, *m*-C), 139.8 (2 C, *s*, *p*-C) 121.2 and 120.9 (2 C, *s*'s, arom.-C-1), 110.6 (4 C, *d*, *o*-C), 79.4 (*d*, C-5), 75.9 (*d*, C-3), 73.2 (*d*, C-2), 71.2 (*d*, C-4), 67.3 (*t*, C-1), 64.9 (*t*, C-6). Octaacetate, mp 155–157°, $[\alpha]_D^{20}$ + 68° (*c* 0.8; Me_2CO). Lit. [2]: mp 154–155°, $[\alpha]_D^{12}$ + 60° (Me_2CO).

Hydrolysis for 24 hr using Amberlite IR-120 (H^+ form) as the catalyst gave gallic acid and 1,5-anhydroglucitol (**1**) both characterized by TLC, and the latter also by comparison of its ^{13}C NMR spectrum with that of an authentic sample: (22.6 MHz, D_2O/DMSO-d_6): δ 81.6 (*d*, C-5), 78.8 (*d*, C-3), 71.0 (*d*, C-4), 70.7 (*d*, C-2), 70.1 (*t*, C-1), 62.2 (*t*, C-6). Assignments were done by selective proton decoupling and are in agreement with published values [3].

Acknowledgements—We thank Dr. N.-G. Treschow, The Botanical Garden, The University of Copenhagen and Dr. J. Rahn, The Botanical Museum, University of Copenhagen for providing and authenticating the *Acer ginnala* (No. 5558/33) material, and The Danish Natural Science Research Council for access to NMR facilities.

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