Tetrahedron Letters No. 18, pp. 1489-1491, 1970. Pergamon Press. Printed in Great Britain.

STRUCTURE OF NEW GIBBERELLIN GLUCOSIDE IN IMMATURE SEEDS OF PHARBITIS NIL

Takao Yokota, Noboru Murofushi and Nobutaka Takahashi
Department of Agricultural Chemistry, The University of Tokyo,
Bunkyo-ku, Tokyo, Japan

(Received in Japan 26 February 1970; received in UK for publication 18 March 1970)

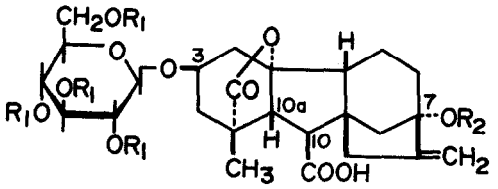
We have isolated seven gibberellin glucosides (1, 2) from immature seeds of morning-glory (Pharbitis nil) and elucidated the structures of six of them (3). Now we wish to report the structure of a new gibberellin glucoside, tentatively termed F-VII.

The enzymatic hydrolysis of F-VII (Sigma's cellulase, 0.2 M acetate buffer, pH 4.5, 37°, 16 hr) yielded its aglycone (IV, amorphous) which was converted to a crystalline monomethyl ester (V) m.p. 197-200°. The high resolution mass spectrum of V showed a parent ion peak at m/e 362.1742 with composition $C_{20}H_{26}O_6$ (calcd. 362.1729) and prominent peaks at M-32, M-46, M-50, M-59, M-60 and M-78 which constitute a characteristic pattern of C_{19} gibberellin methyl esters (4, 5). In the NMR spectrum of V (in D_6-acetone) an AB quartet due to the C-10, C-10a protons characteristic of the gibbane ring was observed at τ 7.27 and 7.44 (J=10 cps). The spectral properties of V showed that the aglycone is a new gibberellin which has the same molecular formula as gibberellin A_1 (GA_1), its C-2 epimer and GA_{16}. Thus the aglycone was named gibberellin A_{29} ($C_{19}H_{24}O_6$). As summarized in Table the functional groups of V are deduced on the basis of the IR and NMR spectra.

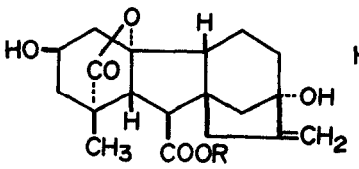
On acid hydrolysis (1N H_2SO_4, 100°, 4 hr), F-VII (I) yielded a keto-acid (VI) m.p. 247-251° and glucose, exclusively. Glucose was identified by gas-liquid chromatography of its trimethylsilyl ether. VI has IR bands (nujol, cm^{-1}) attributable to hydroxyl (3260), γ-lactone (1780), five-membered ring ketone (1740) and carboxyl (2600 and 1700) groups. VI formed a monomethyl ester (VII) m.p. 214°, the mass spectrum of which showed a parent ion peak at m/e 362

Table Functional Groups in GA_{29} Methyl Ester

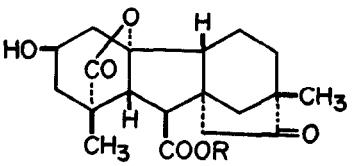
		IR (cm^{-1}, nujol)	NMR (τ, in D_6-acetone)
2	OH	3240	
1	γ-lactone	1790	
1	$COOCH_3$	1750	6.28 (3H, s)
1	$>C=CH_2$	1660	4.82, 5.16 (1H, broad s)
1	$-\overset{|}{C}-CH_3$		8.94 (3H, s)



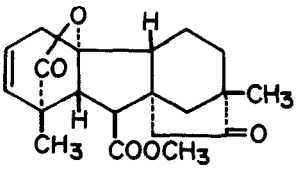
I $R_1=R_2=H$
II $R_1=COCH_3$, $R_2=H$
III $R_1=R_2=COCH_3$



IV R=H
V R=CH_3



VI R=H
VII R=CH_3



VIII

($C_{20}H_{26}O_6$). The above data suggest that VI was formed from the aglycone (GA_{29}) through Wagner-Meerwein rearrangement of the C, D rings (6, 7). To enable such rearrangement GA_{29} must have a C-7 hydroxyl group. The NMR spectrum (in $CDCl_3$) of VII showed a 1H multiplet (band width=35 cps) at τ 5.99 due to $\underline{H}-\overset{|}{C}-OH$ type, at least eleven lines being observed. This is interpreted only by the location of a hydroxyl group at C-3 in an equatorial conformation. The low τ value of the proton can be ascribed to the influence of the C-4a oxygen in 1,3-diaxial relationship. Thus the structures of IV and VI were assigned to GA_{29} and the keto-acid. These were further confirmed by the following chemical conversion. The monomesylate of VII obtained on the treatment with pyridine and mesyl chlo-

ride was refluxed in collidine for 7 hr. The product purified by thin-layer chromatography was crystallized into plates, m.p. 163°, which were identified as the known substance (VIII) derived from GA_5 methyl ester on acid treatment (7).

On acetylation F-VII afforded a tetraacetate (II) m.p. 258-263° which was converted to a pentaacetate (III) m.p. 269-272° having no hydroxyl group on the prolonged treatment. Accordingly it is clear that F-VII has a free tertiary hydroxyl group at C-7. Since the NMR spectra of II and III (in $CDCl_3$) showed a β-anomeric proton at τ 5.52 (doublet, J=7.5 cps), the glucose moiety must be connected to the C-3 hydroxyl group by β-glucosidic linkage. Mass spectra of the trimethylsilyl ether and the pentaacetate of F-VII methyl ester showed the parent ion peaks at m/e 884 and 734, respectively, indicating that F-VII is composed of each one mole of GA_{29} and glucose. Thus the structure I, 3-O-β-glucosyl-gibberellin A_{29}, can be assigned to F-VII.

Acknowledgement. We thank Dr. Y. Sumiki, Professor Emeritus, and Professor S. Tamura, The University of Tokyo, for their interests in this study. We also express our thanks to Professor M. Katsumi, International Christian University, Tokyo, for the enzymatic hydrolysis, Sankyo Co. Ltd., Tokyo, for the high resolution mass spectrum and Mr. K. Aizawa, this Department, for the NMR spectra.

References

1. S. Tamura, N. Takahashi, T. Yokota, N. Murofushi and Y. Ogawa, Planta (Berl.), 78, 208, 1968.
2. T. Yokota, N. Takahashi, N. Murofushi and S. Tamura, ibid., 87, 180, 1969.
3. T. Yokota, N. Takahashi, N. Murofushi and S. Tamura, Tetrahedron Letters, 1969, 2081.
4. N. Takahashi, N. Murofushi, S. Tamura, N. Wasada, H. Hoshino, T. Tsuchiya, S. Sasaki, T. Aoyama and E. Watanabe, Org. Mass. Spect., 2, 711, 1969.
5. R. Binks, J. MacMillan and R. J. Pryce, Phytochemistry, 8, 271, 1969.
6. N. Takahashi, Y. Seta, H. Kitamura, A. Kawarada and Y. Sumiki, Bull. Agric. Chem. Soc. Japan, 21, 75, 1957.
7. J. MacMillan, J. C. Seaton and P. J. Suter, Tetrahedron, 11, 60, 1960.