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Synthesis of GA_{20} Glucosyl Derivatives and the Biological Activity of Some Gibberellin Conjugates

G. Schneider,[1] G. Sembdner,[1] and B. O. Phinney[2]

[1]Institute of Plant Biochemistry, Halle (Saale), G.D.R., Research Centre for Molecular Biology and Medicine, Academy of Sciences of the German Democratic Republic, and [2]Department of Biology, University of California, Los Angeles, California, USA

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Abstract. GA_{20}-13-0-glucoside (*7a*) and GA_{20} glucosyl ester (*6a*), potential endogenous conjugates in maize, were synthesized chemically. The biological activities of these compounds and of nine more GA glucosyl derivatives were determined using the *Zea mays dwarf-5* seedling and *Oryza sativa* cv. "*Tan-ginbozu*" assays. The relative bioactivities of the conjugates were also calculated.

Gibberellins (GAs) are known to be involved in the regulation of many physiological processes in plants. Qualitative as well as quantitative changes of the GA content are assumed to parallel physiological effects. Thus, both identification and quantification of all GAs in a plant are necessary in order to study the mechanism of regulation (Metzger and Zeevaart 1980, Hedden et al. 1982, Yamaguchi et al. 1982). While recent studies have taken into account the kinds and amounts of free GAs, GA conjugates have received little attention, even though they may sometimes represent the major endogenous GA content or represent the main products from feeding experiments (e.g., Yamane et al. 1975, Rood et al. 1982). This situation is the result of difficulties in analyzing trace amounts of highly polar substances—e.g., GA glucosyl derivatives. Also, the physical and biological properties of only a few of the derivatives are known. A cautious interpretation has to be made of the released free GAs that come from the enzymatic or chemical hydrolysis of GA conjugates (Schneider 1983).

We became interested in GA conjugation in maize, and especially GA_{20},

Abbreviations: GA, gibberellin; ^{1}H NMR, proton nuclear magnetic resonance; TMS, tetramethylsilane; HPLC, high-performance liquid chromatography.

because of recent studies on the content and metabolism of GAs in *Zea mays* (Hedden et al. 1982, Heupel et al. 1982, Wurtele et al. 1982, Phinney and Spray 1982). GA_{20} is the gibberellin immediately prior to GA_1, and GA_1 is probably the only active gibberellin per se in maize (Phinney and Spray 1982). Channeling GA_{20} into a conjugate could be an important way of regulating the level of free GA_1. In this study we report the synthesis of two GA_{20} glucosyl derivatives together with information on the bioactivities of nine GA glucosyl derivatives.

Materials and Methods

Synthesis of GA_{20}-13-0-glucoside (7a)

Gibberellin A_{20} methyl ester (*5b*) (560 mg, 1.6 mmole) (Beale et al. 1980) and Ag_2CO_3/celite (5.8 g, ca. 10 mmole) in dichloroethane (30 ml) were reacted for 15 min with α-acetobromoglucose (3.5 g, 8.0 mmole) dissolved in dichloroethane (2 ml) under reflux (Schneider 1981a,b). The filtered and evaporated mixture was deacetylated by 25 ml of 0.5 N sodium methoxide (1 h at room temperature). Subsequent column chromatography on 60 g silica eluted with chloroform containing 0, 5, 10, 15, 20, 25% methanol (150 ml each concentration, 50-ml fractions) gave unreacted GA_{20} methyl ester (*5b*) (220 mg = 58.9% yield) in fractions 4–8 and GA_{20}-13-0-glucoside methyl ester (*7b*) (322 mg = 39.8% yield) in fractions 12–15.

The methyl ester of GA_{20}-13-0-glucoside (*7b*) (300 mg, 0.59 mmole) was treated with lithium propyl thiolate (3.2 mmole) in hexamethyl phosphoramide under nitrogen for 3 h. Column chromatography on 30 g silica (chloroform:methanol:acetic acid; 50:0:0, 45:5:0, 40:10:1, 40:10:2, 40:10:4, 15 ml-fractions) yielded 226 mg amorphous GA_{20}-13-0-glucoside (*7a*) in fractions 11–14 (77.5% yield, total yield 30.9%). ^1H NMR (acetone-D_6/TMS): 1.03 (s, 18-H_3), 2.589 (m, 5- and 6-H), 4.553 (d, J = 7.7 Hz, 1-H), 4.953 and 5.322 ppm (m, 17-H_2).

Synthesis of GA_{20} glucosyl ester (6a)

Gibberellin A_{20} (*5a*) (50 mg, 0.15 mmol) (Beale et al. 1980) and Ag_2CO_3/celite (95 mg, ca. 0.17 mmole) in dichloroethane (4 ml) was stirred and heated. A solution of α-acetobromoglucose (65 mg, 0.16 mmole) in dichloroethane (1 ml) was added. After 10 min the mixture was filtered, the solvent evaporated, and the residue, dissolved in methanol, applied to a 15-ml DEAE-Sephadex A-25 column. The column was eluted stepwise with 15-ml aliquots of methanol, 0.5 N acetic acid-methanol, 1.0 N acetic acid/methanol, 3.0 N acetic acid/methanol; 5 ml fractions were collected.

Fractions 3–5 contained a neutral mixture, which was rechromatographed on a column of 8 g silica with petroleum ether/ethyl acetate, giving 48 mg GA_{20}-β-D-2,3,4,6-tetra-0-acetyl-glucosyl ester (*6b*) (49% yield); crystals from methanol, m.p. 142–144° decomp. Fractions 13–14 contained 25 mg (48%) of un-

reacted GA_{20} (*5a*); (*6b*) (28 mg, 0.04 mmole) in methanol (1 ml) was reacted with 0.5 N sodium methoxide (30 μl) for 5 min at room temperature. The crude mixture was separated on TLC (silica; chloroform:methanol:water:acetic acid; 80:30:2:5). Elution of the zone of R_f = 0.8–0.6 with methanol, followed by redissolving in acetone, gave 12 mg of GA_{20}-β-D-glucosyl ester (*6a*) (57%; total yield = 28.0%). ^1H NMR (acetone-D_6/TMS): 1.027 (s, 18-H_3), 2.608 (d, J = 10.26 Hz, 6-H), 2.689 (d, J = 10.26 Hz, 5-H), 4.850 and 5.174 (m, 17-H_2), 5.535 ppm (d, J = 7.72 Hz, 1-H).

HPLC Conditions

A Serva Si-polyol C-18 column (4.6 × 250 mm) was fitted with an RCT HPLC eluent supply and a Pye/Philips PU 4020 detector set on 206 nm. Isocratic elution with methanol:0.1% phosphoric acid (1 ml/min) was used; 2–5 μg of each compound per injection was applied.

Dwarf-5 *Maize Assay*

The experimental details of the *dwarf*-5 maize assay used in these studies have been described previously (Phinney and Spray 1982).

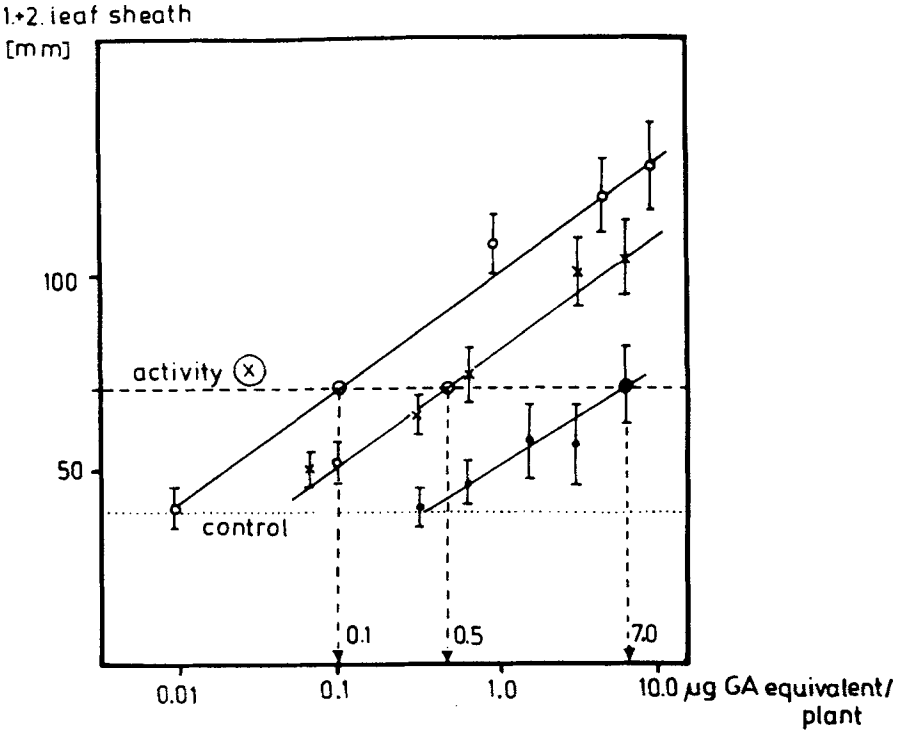
Dwarf Rice Assay (cv. "Tan-ginbozu")

The bioassay was performed according to Sembdner et al. (1976). Substances were applied via the roots.

Results and Discussion

Gibberellin A_{20} (*5a*) and GA_{20} methyl ester (*5b*) (Fig. 1) were reacted with α-acetobromoglucose in the presence of silver carbonate/celite (Schneider 1981a,b). In the case of GA_{20} methyl ester (*5b*) the 13-hydroxyl group was glucosylated with a yield of 39.8%, resulting in GA_{20}-13-0-glucoside methyl ester (*7b*). Demethylation of (*7b*) gave GA_{20}-13-0-glucoside (*7a*) with a total yield of 30.9%. The doublet at 4.553 ppm (J = 7.7 Hz) in the ^1H NMR spectrum confirms the β-D-glucopyranoside structure.

The reaction of equivalent amounts of free GA_{20} (*5a*) and α-acetobromoglucose under the same conditions led to the ester tetraacetate (*6b*) (m.p. 142–144°), which by short-term deacetylation gave GA_{20} glucosyl ester (*6a*) (28% total yield), showing the characteristic 1-H doublet at 5.535 ppm (J = 7.72 Hz) for the glucosyl ester linkage in the ^1H NMR. The purity of the synthesized conjugates was checked by reverse-phase HPLC (Table 1) (Schneider 1983, Koshioka et al. 1983). The results show that reverse-phase HPLC is capable of discriminating glucosides and glucosyl esters as well as other interfering conjugates. However, a comparison of the data reveals that the chromatographic behavior of unknown conjugates can rarely to predicted. For example,



	GA_{20}	GA_{20} glucosyl ester	GA_{20}-13-O-glucoside	
activity ⊗	0.1	0.5	7.0	µg GA_{20} equivalent
relative activity	100	20	1.4	%

Fig. 1. Log:normal dose:response curves of GA_{20} (*5a*)—○—, GA_{20} glucosyl ester (*6a*)—x—, and GA_{20}-13-0-glucoside (*7a*)—●—of the *dwarf*-5 assay and calculations of the "relative activities."

GA_1, GA_5, and GA_{20} glucosides (*1c, 1d, 3c, 7a*) elute prior to the glucosyl esters (*1b, 3b, 6a*), whereas the glucosyl conjugates of GA_4 (*2b, 2c*) and GA_7 (*4b, 4c*) show the opposite pattern.

Gibberellin A_{20}-13-0-glucoside (*7a*) and GA_{20} glucosyl ester (*6a*) are likely to occur endogenously. Their presence has been assumed in polar fractions after feeding GA_{20} to various plants (Frydman and MacMillan 1975, Durley et al. 1975, Yamane et al. 1975, 1977, Takahashi et al. 1976, Rood et al. 1982).

The significance of the bioactivities of GA conjugates is difficult to assess, since the observed responses may be due to hydrolysis of the sugar moiety and liberation of "free" gibberellin. For this reason it has been stated that GA conjugates per se are biologically inactive (Sembdner et al. 1980, Schneider 1983). There are some examples where the observed bioactivities apparently parallel the percentage of free GA released (Hiraga et al. 1974, Liebisch 1974).

Table 1. Retention times (Rt), capacity factors (K'), and number of theoretical plates (N) of GA glucosyl conjugates and their parent GAs on reverse-phase chromatography (Si Polyol C_{18}), 1 ml min^{-1}; methanol: 0.1% phosphoric acid = 55:45 (v:v).

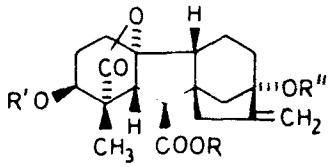
	Rt	K'	N
GA_1 (1a)	3.82	0.75	3,300
GA_1 glucosyl ether (*1b*)[a]	3.50	0.60	1,830
GA_1-3-0-glucoside (*1c*)[b]	3.23	0.48	1,500
GA_1-13-0-glucoside (*1d*)[b]	3.13	0.44	1,000
GA_4 (*2a*)	14.45	5.63	3,340
GA_4 glucosyl ester (*2b*)[a]	7.42	2.40	1,640
GA_4-3-0-glucoside (*2c*)[b]	10.97	4.03	2,770
GA_5 (*3a*)	6.20	1.84	2,160
GA_5 glucosyl ester (*3b*)[c]	4.58	1.10	2,500
GA_5-13-0-glucoside (*3c*)[b]	4.18	0.89	2,460
GA_7 (*4a*)	12.50	4.73	3,600
GA_7 glucosyl ester (*4b*)[d]	6.25	1.87	2,750
GA_7-3-0-glucoside (*4c*)[e]	10.03	3.60	2,520
GA_{20} (*5a*)	6.25	1.87	2,200
GA_{20} glucosyl ester (*6a*)	5.17	1.37	1,960
GA_{20}-13-0-glucoside (*7a*)	4.25	0.95	2,600

[a] Synthesized according to Hiraga et al. (1974).
[b] Schneider et al. (1977b).
[c] Schneider et al. (1977a).
[d] Schneider et al. (1984).
[e] Schneider (1981b).

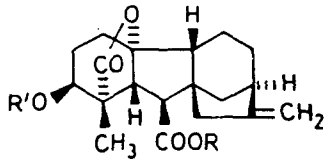
For this reason the activity of a GA conjugate should be compared only to the activity of the parent GA. In this approach the aglycone (GA) activity would be set at 100%, and the relative activities calculated from log-normal dose-response curves of both the aglycone and the conjugate. Comparison should be made of straight and parallel segments of the curves (Fig. 1).

Table 2 shows that all the GAs tested (GA_1, GA_4, GA_5, GA_7, GA_{20}) are highly active in the *dwarf*-5 assay. The relative activities of all investigated glucosides of these GAs ranged from 1% to 5%. Assuming that each conjugate is inactive per se, only small percentages of the applied conjugates were hydrolyzed to give free, biologically active GAs. Our results support those of earlier studies on the activity of GA glucosides in maize and other bioassays that use the leaf as the site of treatment (Yokota et al. 1971, Sembdner et al. 1976). There are also no striking differences in activity between GA-3-0-glucosides and GA-13-0-glucosides, although these types were found to differ in their susceptibility to cellulase (Schliemann and Schneider 1979, Schneider and Schliemann 1979).

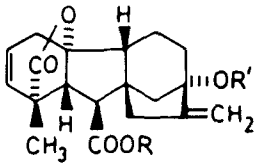
Relative bioactivities of 1% to 100% have been reported for the GA glucosyl esters of GA_1, GA_3, GA_4, GA_{37} (Hiraga et al. 1974). In our experiments the highest relative activity (50%) was found for GA_4 glucosyl ester (*2b*) (Table 2). All other investigated glucosyl esters were less active (10–20%) than (*2b*) but clearly more active than the corresponding glucosides. This could mean that



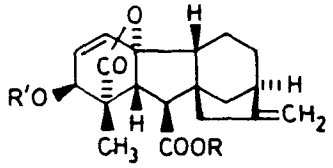
1a: R = R' = R'' = H
1b: R = Glc, R' = R'' = H
1c: R = R'' = H, R' = Glc
1d: R = R' = H, R'' = Glc



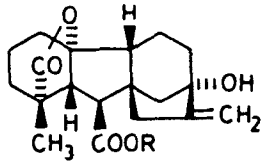
2a: R = R' = H
2b: R = Glc, R' = H
2c: R = H, R' = Glc



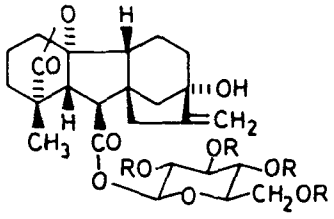
3a: R = R' = H
3b: R = Glc, R' = H
3c: R = H, R' = Glc



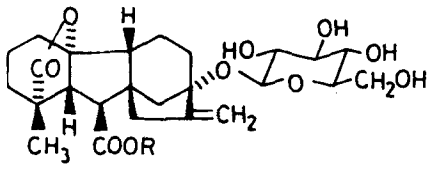
4a: R = R' = H
4b: R = Glc, R' = H
4c: R = H, R' = Glc



5a: R = H
5b: R = CH_3



6a: R = H
6b: R = Ac



7a: R = H
7b: R = CH_3

Fig. 2. Chemical structures of compounds referred to in the text.

Table 2. Bioassay of GA glucosides, GA glucosyl esters, and the parent GAs on *dwarf*-5 (μg/plant). Data are given as length (mm) of the first and second leaf sheath confidence limit as well as "relative activity" (%).

	10 μg	5 μg	1 μg	0.5 μg	0.1 μg	Control	Relative activity (%)
GA_1 (*1a*)	128 ± 17	127 ± 10	103 ± 15	88 ± 12	62 ± 3	45 ± 4	100
GA_1 glucosyl ester (*1b*)	90 ± 10	72 ± 10	61 ± 6	52 ± 4	43 ± 3	41 ± 2	10
GA_1-3-0-glucoside (*1c*)	50 ± 4	51 ± 7	62 ± 5	54 ± 3	48 ± 3	43 ± 2	<1
GA_1-13-0-glucoside (*1d*)	70 ± 7	60 ± 6	61 ± 6	47 ± 6	—	41 ± 2	2–5
GA_4 (*2a*)	133 ± 16	110 ± 15	88 ± 14	66 ± 10	50 ± 4	35 ± 3	100
GA_4 glucosyl ester (*2b*)	100 ± 10	96 ± 8	75 ± 14	64 ± 14	44 ± 4	38 ± 3	50
GA_4-3-0-glucoside (*2c*)	55 ± 6	54 ± 8	44 ± 3	41 ± 2	36 ± 4	38 ± 4	1–5
GA_5 (*3a*)	136 ± 9	138 ± 15	110 ± 20	98 ± 14	69 ± 6	37 ± 3	100
GA_5 glucosyl ester (*3b*)	73 ± 12	81 ± 10	68 ± 7	55 ± 8	42 ± 6	26 ± 4	5–10
GA_5-13-0-glucoside (*3c*)	61 ± 6	54 ± 10	44 ± 7	38 ± 4	32 ± 3	27 ± 3	1
GA_7 (*4a*)	113 ± 8	112 ± 9	96 ± 14	91 ± 16	76 ± 18	17 ± 2	100
GA_7 glucosyl ester (*4b*)	96 ± 22	90 ± 22	66 ± 15	60 ± 15	46 ± 12	17 ± 2	10
GA_7-3-0-glucoside (*4c*)	52 ± 11	47 ± 12	36 ± 5	29 ± 7	19 ± 3	17 ± 2	<1
GA_{20} (*5a*)	128 ± 12	120 ± 10	109 ± 10	—	51 ± 6	37 ± 3	100
GA_{20} glucosyl ester (*6a*)	104 ± 11	101 ± 16	74 ± 6	64 ± 5	50 ± 4	40 ± 3	20
GA_{20}-13-0-glucoside (*7a*)	72 ± 12	56 ± 9	46 ± 6	40 ± 4	—	35 ± 1	1–3

Table 3. Bioassay of some GA glucosides, GA glucosyl esters, and the parent GAs on dwarf rice cv. "*Tan-ginbozu*"; data are given as length (mm) of the seedling ± confidence limit.

	10^{-4}	10^{-5}	10^{-6}	10^{-7} molar
GA_1 (*1a*)	132 ± 42	91 ± 5	47 ± 13	30 ± 4
GA_1 glucosyl ester (*1b*)	137 ± 49	93 ± 27	43 ± 12	32 ± 7
GA_1-13-0-glucoside (*1c*)	120 ± 48	84 ± 36	41 ± 10	32 ± 5
GA_1-13-0-glucoside (*1d*)	143 ± 16	77 ± 29	40 ± 2	28 ± 5
GA_4 (*2a*)	125 ± 17	46 ± 5	42 ± 4	24 ± 4
GA_4 glucosyl ester (*2b*)	106 ± 32	53 ± 5	36 ± 3	30 ± 7
GA_4-3-0-glucoside (*2c*)	116 ± 23	50 ± 6	34 ± 4	22 ± 3
GA_5 (*3a*)	117 ± 29	81 ± 35	77 ± 38	42 ± 8
GA_5 glucosyl ester (*3b*)	128 ± 33	76 ± 22	65 ± 22	37 ± 7
GA_5-13-0-glucoside (*3c*)	122 ± 20	86 ± 21	71 ± 26	36 ± 8
GA_7 (*4a*)	122 ± 23	65 ± 7	40 ± 4	29 ± 6
GA_7 glucosyl ester (*4b*)	152 ± 38	69 ± 16	44 ± 4	33 ± 5
GA_7-3-0-glucoside (*4c*)	141 ± 28	72 ± 26	48 ± 8	32 ± 6
GA_{20} (*5a*)	113 ± 14	87 ± 27	51 ± 14	36 ± 4
GA_{20} glucosyl ester (*6a*)	103 ± 36	96 ± 29	49 ± 12	35 ± 3
GA_{20}-13-0-glucoside (*7a*)	110 ± 16	90 ± 23	52 ± 9	29 ± 6
GA_3	140 ± 36	133 ± 28	95 ± 12	39 ± 9
Water control		29 ± 5		

GA glucosyl esters, like their glucosides, are only partially hydrolyzed in the *dwarf*-5 assay to liberate free GAs (Liebisch 1974).

In the rice bioassay, where substances were applied via the roots, enzymes in the medium are apparently present that hydrolyze GA glucosyl conjugates. As a result high biological activities were observed for all compounds tested (Table 3). The dwarf rice assay is thus useful for the initial localization of GA glucosyl conjugates in crude or partially purified extracts.

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References

Beale MH, Gaskin P, Kirkwood P, MacMillan J (1980) Partial synthesis of gibberellin A_9 and [3α and 3β-$^2H_1$] gibberellin A_9, gibberellin A_5 and [1β,3-$^2H_2$ and $^3H_2$]gibberellin A_5, and gibberellin A_{20} and [1β, 3α $^2H_2$ and $^3H_2$]gibberellin A_{20}. J Chem Soc Perkin I 1980:885–891

Durley AC, Pharis RP, Zeevaart JAD (1975) Metabolism of [^{3}H]gibberellin A_{20} by plants of *Bryophyllum daigremontianum* under long and short day conditions. Planta 126:139–149

Frydman VM, MacMillan J (1975) The metabolism of gibberellins A_9, A_{20} and A_{29} in immature seeds of *Pisum sativum* cv. 'Progress No. 9.' Planta 125:181–195

Hedden P, Phinney BO, Heupel R, Fujii D, Cohen H, Gaskin P, MacMillan J, Graebe JE (1982) Hormones of young tassels of *Zea Mays*. Phytochemistry 21:391–393

Heupel R, Phinney BO, Hedden P (1982) Metabolism of [^{14}C] and [^{3}H]GA_{53} in *Zea mays*. In: Abstracts of the Symposium on Biochemistry and Function of Isopentenoids in Plants, Berkeley, California, March 22–24, 1982:23

Hiraga K, Yamane H, Takahashi N (1974) Biological activity of some synthetic gibberellin glucosyl esters. Phytochemistry 13:2371–2376

Koshioka M, Harada J, Takeno K, Noma M, Sassa T, Ogiyama K, Taylor JS, Rood SB, Legge RL, Pharis RP (1983) Reverse phase C_{18} high-performance liquid chromatography of acidic and conjugated gibberellins. J Chromatogr 256:101–115

Liebisch HW (1974) Uptake, translocation and metabolism of labelled GA_3 glucosyl ester. In: Schreiber K, Schütte MR, Sembdner G (eds) Biochemistry and chemistry of plant growth regulators. Institute of Plant Biochemistry, Halle, pp 109–113

Metzger JD, Zeevaart JAD (1980) Comparison of the level of six endogenous gibberellins in roots and shoots of spinach in relation to photoperiods. Plant Physiol 66:679–682

Phinney BO, Spray C (1982) Chemical genetics and the gibberellin pathway in *Zea mays* L. In: Wareing PF (ed) Plant growth substances 1982. Academic Press, London, pp 101–110

Rood B, Koshioka M, Douglas TJ, Pharis RP (1982) Metabolism of tritiated gibberellin A_{20} in maize. Plant Physiol 70:1614–1618

Schliemann W, Schneider G (1979) Untersuchungen zur enzymatischen Hydrolyse von Gibberellin-0-glucosiden. I. Hydrolysege-schwindigkeiten von Gibberellin-13-0-glucosiden. Biochem Physiol Pflanzen 174:739–745

Schneider G (1981a) Synthese von Gibberellinglucosiden. Dissertation BAdW der DDR, Berlin

Schneider G (1981b) Uber strukturelle Einflusse bei der Glucosylierung von Gibberellinen. Tetrahedron Lett 37:545–549

Schneider G (1983) Gibberellin conjugates. In: Crozier A (ed) The biochemistry and physiology of gibberellins, Vol 1, Praeger, New York, pp 389–456

Schneider G, Schliemann W (1979) Untersuchungen zur enzymatischen Hydrolyse von Gibberellin-0-glucosiden. II. Hydrolysege-schwindigkeiten von Gibberellin-2-0- und Gibberellin-3-0-glucosiden. Biochem Physiol Pflanzen 174:746–751

Schneider G, Miersch O, Liebisch HW (1977a) Synthese von 0-β-D-Glucopyranosyl-gibberellin-0-β-D-glucopyranosylestern. Tetrahedron Lett 1977:405–406

Schneider G, Sembdner G, Schreiber K (1977b) Syntheses von 0(3)- und 0(13)-glucosylierten Gibberellinen. Tetrahedron Lett 33:1391–1397

Schneider G, Sembdner G, Phinney BO, Schreiber K (1984) Chemical synthesis of some physiologically relevant gibberellin glucosyl conjugates. Tetrahedron Lett (in press)

Sembdner G, Borgmann E, Schneider G, Liebisch HW, Miersch O, Adam G, Lischewski M, Schreiber K (1976) Biological activity of some conjugated gibberellins. Planta 132:249–257

Sembdner G, Gross D, Liebisch HW, Schneider G (1980) Biosynthesis and metabolism of plant hormones. In: MacMillan J (ed) Encyclopedia of plant physiology, new series, Vol 9. Springer-Verlag, Berlin, pp 281–444

Takahashi N, Murofushi N, Yamane H (1976) Metabolism of gibberellins in maturing and germinating bean seeds. Plant Growth Substances 1976:383–385

Wurtele ES, Hedden P, Phinney BO (1982) Metabolism of the gibberellin precursors *ent*-kaurene, *ent*-kaurenol, and *ent*-kaurenal in a cell-free system from seedling shoots of normal maize. J Plant Growth Regul 1:15–24

Yamaguchi I, Fujisawa S, Takahashi N (1982) Qualitative and semiquantitative analysis of gibberellins. Phytochemistry 21:2049–2055

Yamane H, Murofushi N, Takahashi N (1975) Metabolism of gibberellins in maturing and germinating bean seeds. Phytochemistry 14:1195–1200

Yamane H, Murofushi N, Osada H, Takahashi N (1977) Metabolism of gibberellin in early immature bean seeds. Phytochemistry 16:831–835

Yokota T, Murofushi N, Takahashi N, Katsumi M (1971) Biological activities of gibberellins and their glucosides in *Pharbitis nil*. Phytochemistry 10:2943–2949