Synthesis of Aryl Cluster Glycosides by Cyclotrimerization of 2-Propynyl Carbohydrate Derivatives

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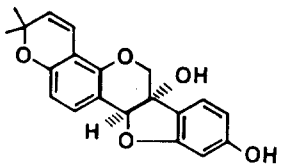
One of the more important responses in plants involves the elicitation of antimicrobial agents called phytoalexins. In some cases the elicitation event is triggered by oligomeric glucan units containing β-1,6 and β-1,3 linkages. Metal ion mediated cyclotrimerization of suitable 2-propynyl sugar precursors was investigated as a method to prepare potential structural analogues of these elicitor molecules. Thus, reaction of the 2-propynyl glucoside **4**, using dicobalt octacarbonyl as catalyst, gave the trimeric cluster glycoside **5a**, in 44% yield. Similarly prepared were the aryl cluster glycosides **16**, **17**, **18**, **19**, **20**, **21**, and **22** from alkynyl precursors **6**, **7**, **8**, **9**, **10**, **12**, **14**, and **15**, respectively. In general, these reactions proceeded with high regioselectivity favoring the 1,2,4 over the 1,3,5 regioisomer by a ratio of 9:1. Hexameric cluster glycosides resulted from the cyclotrimerization of bifunctionally substituted alkynes, **30a**, **32**, and **38** being obtained from **29**, **31**, and **37**, respectively. The aryl cluster glycosides were determined to be inactive as phytoalexin elicitors by the soybean cotyledon bioassay.

Plants respond dynamically to pathogen invasions by changing the types and distribution of secondary metabolites within and adjacent to the invaded tissue.[1] Of these responses, the best understood at the molecular level is the phytoalexin-elicitor system.[2] Phytoalexins are low-molecular-weight antibiotics produced in plants in response to certain fungal and bacterial invasions. Depending upon the plant species, phytoalexins may be isoflavonoids, sesquiterpenes, furanoterpenoids, polyacetylenes, and dihydrophenanthrenes.[3]

Recently, Albersheim et al. have characterized a biotic elicitor that is composed of fragments of polysaccharides present in the mycelial walls of many fungi.[4] These oligomers are believed to be β-1,6-glucans that have additional sugar residues linked at the 3-position of the glucose moieties. Glucan elicitor can be obtained by partial acid hydrolysis of mycelial walls of the fungal pathogen of soybeans, viz., *Phytophthora megasperma* f. sp. *glycinea* (Pmg). The isolated glucan elicitor is very active in stimulating phytoalexin accumulation in soybean tissues. Thus, concentrations of 1 μg/mL are sufficient to stimulate the accumulation of the phytoalexin glyceollin **1** in cotyledons, hypocotyls, and cell suspension cultures of soybeans.[4] If



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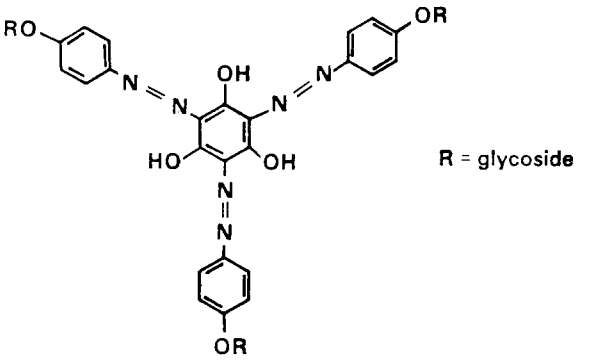
the polymeric glucan elicitor is partially hydrolyzed with acid, oligomeric elicitor-active glucans are produced. The smallest β-glucan fragments that have elicitor activity contain approximately nine β-glycosyl residues interconnected by 1,6- and 3,6-glucosidic linkages.[4]

The exact mechanism by which elicitation occurs is open to conjecture; current speculation is that at least two units of the carbohydrate hapten are involved in the recognition that triggers the biosynthetic events. This model is supported by the fact that the monosaccharide α-methyl mannoside inhibits, but does not trigger, the production of phytoalexins, implying the need for at least two hapten units in the recognition events leading to elicitation.[5]

Inasmuch as only a few of the carbohydrate residues are involved in the actual binding–recognition process, presumably, the remaining sugars in the polymer function as a structural matrix, spacing the haptens at correct distances for interaction with the binding site. Conceivably, structural analogues of elicitors could result from molecules containing an aromatic core supporting pendant sugar haptens. By substitution of structural sugar components with benzenoid groups, the rigidity of the polymeric matrix would be preserved with only minimal distortion to the three-dimensional framework.

The closest analogy to such "aromatic core" cluster glucosides is provided by the well-known Yariv "artificial antigens" **2**, so called because they form brightly colored precipitates with protein antibodies to appropriate carbohydrate determinants.[6] These artificial antigens ag-



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gregate in aqueous solution and act as multivalent haptens binding antibodies to give insoluble three-dimensional networks characteristic of the familiar antibody–antigen interaction.[7]

(1) Kuc, J. A. *Ann. Rev. Phytopathol.* **1972**, *10*, 207.
(2) Kuc, J. A. "*Encyclopedia of Plant Physiology*"; Heitefuss, R.; Williams, P. H., Eds.; Springer: Berlin, 1976; Vol. 4, p 632.
(3) Grisebach, H.; Ebel, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 635.
(4) Albersheim, P.; Valent, B. S. *J. Cell Biol.* **1978**, *78*, 627 and references cited therein.
(5) Ayers, A. R.; Valent, B.; Ebel, J.; Albersheim, P. *Plant Physiol.* **1976**, *57*, 766.
(6) Yarov. J.; Rapport, M. M.; Graf, L. *J. Biochem.* **1962**, *85*, 383.
(7) Wood, E. F.; Lilley, G. G.; Jermyn, M. A. *Aust. J. Chem.* **1978**, *31*, 2225.

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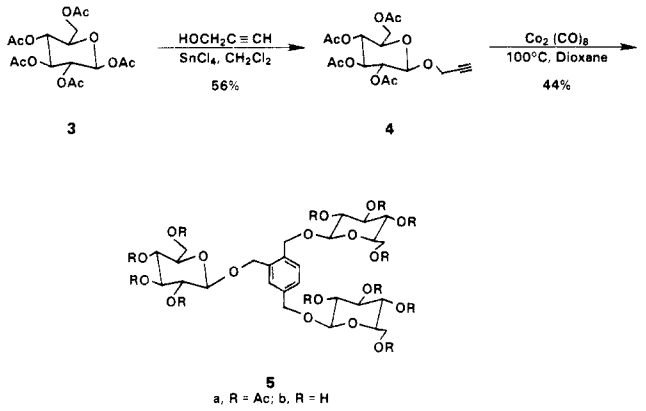
Table I. Cyclotrimerization of 2-Propynyl Sugar Derivatives

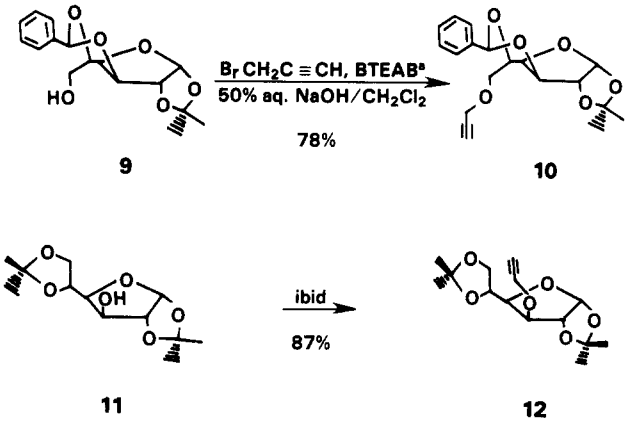
entry	2-propynyl sugar derivative	rctn time, days	CTPM[a] no.	CTPM[a] 1,2,4-	CTPM[a] 1,3,5-	% yield
1	4	4.6	5	100	0	44
2	6:[b] 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-	21	16	90	10	30
3	7:[c] 2,3,4,6-tetra-*O*-α/β-D-galactopyranosyl-	5.5	17[d]			41
4	8: 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl	4.2	18	92	8	61
5	10	7	19	100	0	47
6	12[b]	35	20	90	10	20
7	14	5	21	89	11	15
8	15	4.8	22	84	16	41

[a] CTPM = cyclotrimerized product mixture. [b] Reaction temperature 140–144 °C. [c] Mixture of α and β isomers (3:7). [d] Regioisomeric composition unknown.

Scheme I

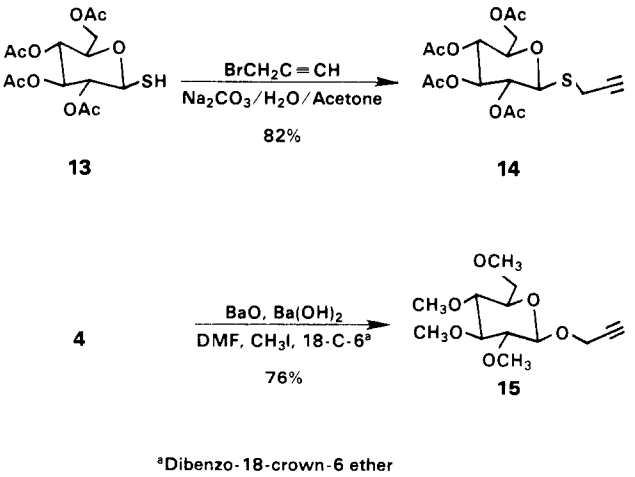


Scheme II



[a] Benzyltriethylammonium bromide

Scheme III



[a] Dibenzo-18-crown-6 ether

The synthesis of the elicitor-type antigens was approached via metal-assisted cyclotrimerization of 2-propynyl glycosides and the results of these investigations are reported below.

Results and Discussion

In searching for viable routes to aromatic cluster glycosides we reasoned that, in principle, such compounds should be accessible from the metal-ion-mediated cyclotrimerization of appropriate acetylenic sugar precursors.[8] To explore the feasibility of this approach, we made 2-propynyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside **4** in 56% yield from **3**, employing the tin tetrachloride catalyzed glycosidation procedure.[9] Treatment of **4** with the cyclotrimerization catalyst, dicobalt octacarbonyl, gave the trimeric cluster glycoside **5a** (R = Ac), which was isolated as a microcrystalline powder after chromatography and crystallization (Scheme I). Inspection of the accumulated spectral and analytical data for **5a** confirmed the assigned structure. The ^{13}C NMR spectrum was most informative, providing direct confirmation for the assigned 1,2,4 regiochemistry of the molecule. The aromatic region of this spectrum showed six absorptions in two sets, the low field set at 136.58, 134.77, and 134.47 ppm representing the quaternary carbon atoms and the high field set at 128.49, 127.79, and 127.09 ppm the tertiary carbon atoms.[10] Deacetylation of **5a** with sodium methylate in methanol gave the triglucoside **5b** (R = H), in quantitative yield.

To further explore the scope and generality of this method, we prepared other acetylenic carbohydrates as follows. 2-Propynyl glucosides (**6**–**8**) were synthesized by

(8) For a review on transition-metal-catalyzed acetylene cyclizations, see Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

(9) (a) Hanessian, S.; Banoub, J. *Methods Carbohydr. Chem.* **1980**, *6*, 243. (b) Lemieux, R. U.; Shyluk, W. P. *Can. J. Chem.* **1953**, *31*, 528. (c) Honma, K.; Nakazima, K.; Uematsu, T.; Hamada, A. *Chem. Pharm. Bull.* **1976**, *24*, 394.

(10) These results were confirmed independently by single-frequency off-resonance decoupling experiments.

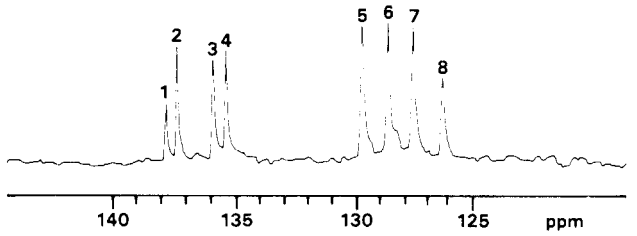


Figure 1. Carbon-13 25-MHz NMR spectrum of **20**, aromatic region. Peaks 2–7 represent the 1,2,4 regioisomer and peaks 1, 8 the 1,3,5 regioisomer.

a procedure similar to that used for **4**; details are provided in the Experimental Section. Compounds **10** and **12** were prepared by phase-transfer-catalyzed alkylation of precursors **9** and **11** (Scheme II). 2-Propynyl 2,3,4,6-tetra-*O*-acetyl-β-D-1-thioglucopyranoside **14** was synthesized by the alkylation of 2,3,4,6-tetra-*O*-acetyl-β-D-1-thioglucopyranose **13** with 2-propynyl bromide and, 2-propynyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside **15** was prepared by the permethylation of 2-propynyl β-D-glucopyranoside generated in situ from **4** (Scheme III).

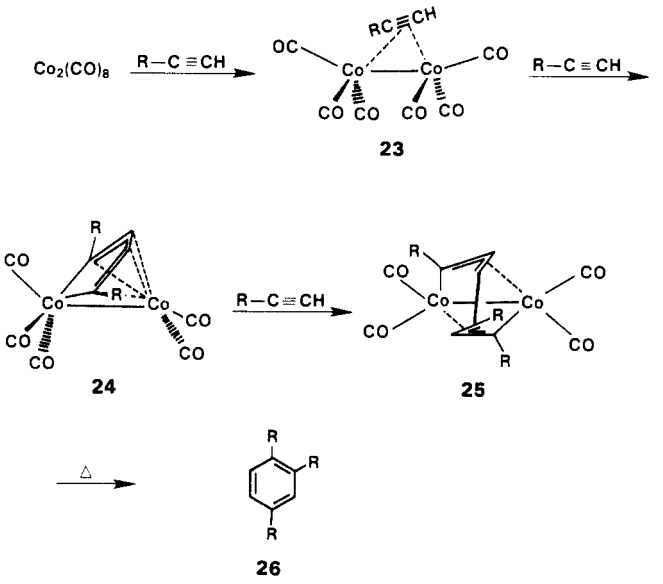
Results obtained from the cyclotrimerization of propynyl sugar derivatives are summarized in Table I. Although the reaction appears to be quite general, the yields (15–61%) tend to be markedly influenced by the nature of the starting material. Sterically encumbered reactants (entries **2** and **6**) reacted slowly under forcing conditions (T = 140 °C) and were usually attended by substantial polymerization, resulting in lowered yields. The thio analogue **14** (entry 7) gave a poor yield of product, undoubtedly due to poisoning of the cobalt catalyst.

Carbon-13 NMR was a useful diagnostic tool in elucidating the regiochemical disposition of cyclotrimerized product mixtures; absorptions due to the central benzene ring of the 1,3,5 regioisomer usually appear as satellites, with reduced intensity, around the six signal core due to the 1,2,4 cyclotrimer. Thus in the case of entry 6, the product mixture showed carbon signals at 138.27 and 125.93 ppm for the 1,3,5 isomer and absorptions at 137.74, 136.14, 135.55, 129.50, 128.33 and 127.24 ppm for the 1,2,4 isomer (Figure 1).

In general, the reactions were found to be highly regioselective, favoring the 1,2,4 over the 1,3,5 isomer; this selectivity was fairly insensitive as to the nature of the starting material. The reason for the regioselectivity of the reaction is not completely clear although it is known that cobalt catalysts tend to favor the 1,2,4 rather than the 1,3,5-trisubstituted benzene.[8] The mechanism of the reaction is believed to be a complex process involving several organometallic species (Scheme IV).[11]

The first intermediate formed under mild conditions is the μ-alkyne complex $Co(CO)_6(R)$ **23**, containing a bridging acetylene ligand. On further heating with excess acetylene, **23** is converted to the complex $Co_2(CO)_5(R)_2$ **24**, which contains a cobalt–cyclopentadiene unit π bonded to the other cobalt atom. Subsequent reaction with acetylene gives the complex $Co_2(CO)_4(R)_3$ **25**, which has been shown by X-ray crystallography to contain a bridging unit linking three alkyne units in a so-called "fly-over" arrangement:[12]

Scheme IV



such complexes thermally degrade to give benzenoid (**26**) and other products.

Recently Bennett et al. have isolated an orange air-stable complex $Co_2(CO)_5(C_8H_{12})_2$ from the reaction of dicobalt octacarbonyl with cyclooctyne and have shown it to have structure **24**, by X-ray analysis.[13] Compound **24** catalyzes the cyclotrimerization of cyclooctyne to tris(hexamethylene)benzene without reversion to $Co(CO)_6(C_8H_{12})_{12}$. Although no fly-over complex can be isolated in this transformation, it is presumed to occur as a transient intermediate. Our findings from the cyclotrimerization of acetylenic sugars are consistent with such a mechanism and implicate **24** as the predominant intermediate in the conversion of such acetylenes to aromatic trisubstituted glycosides.[14]

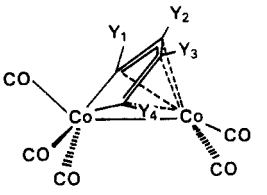
Encouraged by the generality and scope of the cyclotrimerization method for the synthesis of aromatic cluster glycosides, we proceeded to further elaborate this chemistry for the preparation of novel "octupus-like" hexakis(glycosides). In addition to their potential as elicitor mimics, such compounds could conceivably serve as guests in host–guest chemistry: a lipophilic core circumambulated by a hydrophilic periphery provides an ideal environment for inclusion compounds with amphilic guests. Other li-

(11) (a) Hübel, W. "Organic Synthesis via Metal Carbonyls"; Wender, I.; Pino, P., Eds.; Interscience: New York, 1968; Vol. 1, p 273. (b) Bowden, F. L.; Lever, A. P. B. *Organomet. Chem. Rev., Sect. A* **1968**, *3*, 227. (c) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323. (d) Kruerke, U.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2829.

(12) (a) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J., Woodward, P. *J. Chem. Soc., Chem, Commun.* **1978**, 221. (b) Dickson, R. S.; Fraser, P. J., Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1972**, 2278.

(13) Bennett, M. A.; Donaldson, P. B. *Inorg. Chem.* **1978**, *17*, 1995.

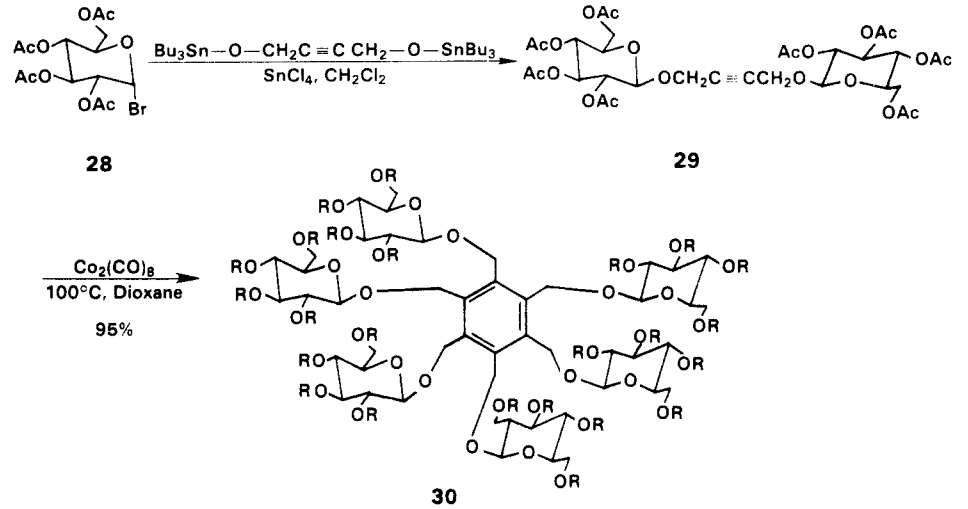
(14) There are four possible isomers (a–d) of the dialkylcobaltacyclopentanoid **24**, two of which are nearly degenerate in energy (b and c).



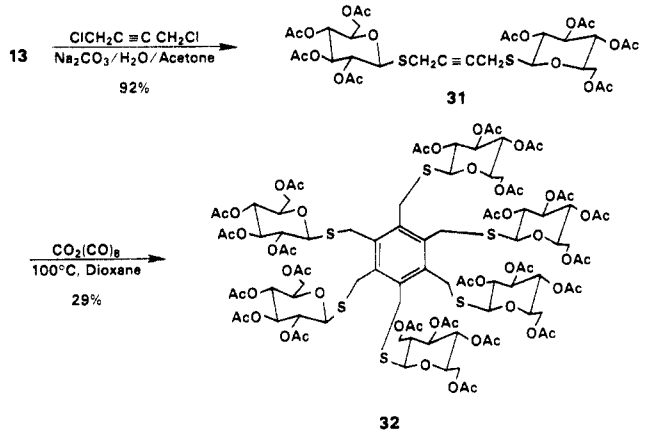
a: Y_1, Y_4 = R; Y_2, Y_3 = H
b: Y_1, Y_3 = R; Y_2, Y_4 = H
c: Y_2, Y_4 = R; Y_1, Y_3 = H
d: Y_2, Y_3 = R; Y_1, Y_4 = H

Statistically, therefore, the 1,2,4 regioisomer is favored over the 1,3,5 isomer by a ratio of 3:1. Steric arguments would predict a 2:1 preponderance of the 1,2,4 isomer assuming **24a**, **24b**, and **24d** are equally favored over **24c**. In any event, an intermediate such as **24** does indeed account for the preferential formation of the 1,2,4 regioisomer.

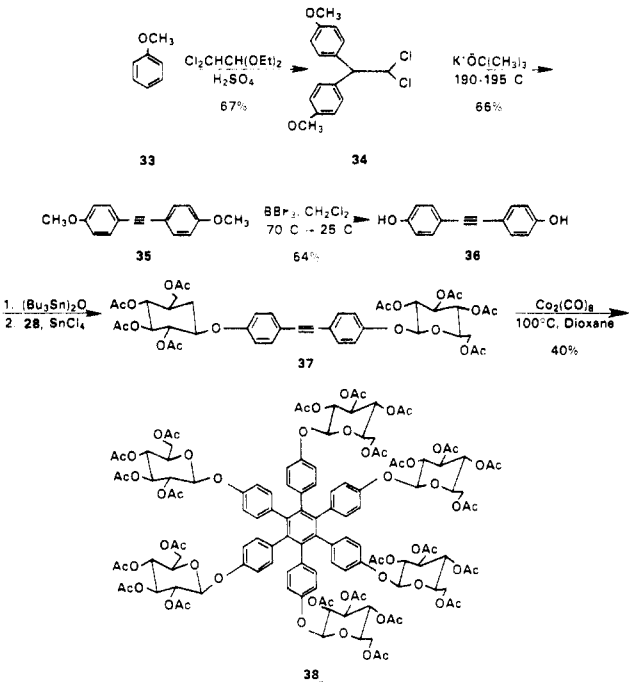
Scheme V



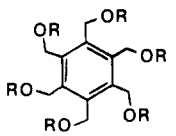
Scheme VI



Scheme VII



pophilic hexaphenyl host molecules are known to favor the formation of inclusion compounds. Thus, compounds of the type **27** form complexes with water, dimethylformamide, diglyme, trichloroethanol, and pyridine.[15]



R = Salicyl, 2-methyl isoquinyl, 2-acetoxyphenyl

27

Hexakis(glycosides) are readily accessible from the corresponding bis(glycoside) monomers. Thus, cyclotrimerization of 2-butyne-1,4-diyl octaacetyl bis(β-D-glucopyranoside) **29** gave benzenehexaylhexamethylene tetraeicosacetyl hexakis(β-D-glucopyranoside) **30a** (R = Ac), in 95% yield after chromatographic purification (Scheme V).

The symmetry of **30a** was confirmed by its decoupled ^{13}C NMR spectrum, which gave one signal for each of the benzenoid and anomeric carbon atoms. The fully coupled ^{13}C NMR spectrum established the quaternary nature of the benzenoid carbon resonance and confirmed the β stereochemistry of the anomeric center ($^2J_{CH}$ = 161.5 HZ).[16] Deacetylation of **30a** gave the deprotected hexakis(glucoside) **30b** (R = H) as a microcrystalline powder, in quantitative yield. The structure of this material was also confirmed by spectral and analytical methods (see Experimental Section).

The thio hexamer **32** was prepared by a similar reaction sequence starting from 2,3,4,6-tetra-*O*-acetyl-β-D-1-thioglucopyranose (**13**; Scheme VI). The spectral properties of **32** were consistent with the assigned structure and require little annotation.

Of the hexakis(glycosides) synthesized, the most intriguing congener was the hexaphenylbenzene derivative **38**. This molecule contains a large hydrophobic core circumscribed by distal sugar units, which provide a unique environment for host–quest chemistry of amphilic molecules. Compound **38** was synthesized starting from 4,4′-dihydroxytolan **36**, which in turn was made by modified literature methods[23] from anisole (**33**; Scheme VII). The tolan **36** was then coupled with the glycosyl bromide **28** to give the bis(glycoside) **37**, which was isolated in moderate yield owing to the sensitivity of **36** to the acidic coupling conditions employed. Cyclotrimerization of **37**

(15) Bever, E.; Muller, W. M.; Vogtle, F. *Tetrahedron Lett.* **1979**, 2335.
(16) Bock, K.; Pedersen, C. *J. Chem. Soc., Perkin Trans 2*, **1974**, 293.

gave **38**, isolated as a microcrystalline, high-melting solid. All spectral and analytical data were consistent with the assigned structure; ^{13}C NMR data confirmed the highly symmetric nature of the molecule.

The bioactivity of the synthetic elicitor analogues was determined by the soybean cotyledon bioassay as developed by P. Albersheim et al.[5] Activity was quantified by measuring inhibition zones to *Cladosporium cucumerinum*—corresponding to the elicited phytoalexin glyceollin (**1**)—in the TLC–fungitoxicity assay.[17] In general, the aryl sugar oligomers were found to be inactive: compounds **4a** and **4b** showed activity corresponding to 5–10% that of the native glucan elicitor as measured in nanomoles of 1 elicited/gram of tissue.

Conclusion

The present study demonstrates that metal ion mediated cyclotrimerization chemistry can be used to advantage in the synthesis of aromatic residues circumscribed by pendant sugar haptens. Although these oligomers afford only weak biological activity relative to their native glucan elicitor counterparts, nevertheless, such sugar cluster provide unique environments for host–guest chemistry of amphipathic molecules. Studies of these properties are underway.

Experimental Section

Proton NMR spectra were recorded at 60 MHz on Varian T-60 and EM-360 spectrometers. Coupled and decoupled ^{13}C NMR spectra were recorded at 25 MHz on a JEOLCO FX-100 instrument; coupling constants obtained using the NOE mode are indicated in parentheses. Unless otherwise stated, NMR spectra were obtained on deuteriochloroform solutions containing Me_4Si (δ = 0) as internal standard: the terms os and brs refer to overlapping singlets and broad singlet, respectively. Melting points were determined on a Laboratory Devices Mel-temp apparatus and are uncorrected. Optical rotations were obtained on a Perkin-Elmer 241MC polarimeter, at 24 °C, and 2% solutions in chloroform (unless otherwise noted). TLC was performed on Baker-Flex precoated silica gel slides; the slides were developed with appropriate mixtures (v/v) of ethyl acetate–hexane (solvent A), ethyl acetate–toluene (solvent B), ethyl acetate–hexane–ethanol (solvent C), and ethyl acetate–toluene–ethanol (solvent D). Visualization was accomplished by spraying with a solution of sulfuric acid in ethanol (20%, v/v), followed by heating to 120 °C for 5 min. HPLC was performed on a Waters Prep-500A instrument with use of the appropriate solvent (vide supra). Elemental analysis were performed by Atlantic Microlabs, Inc. and Galbraith Laboratory.

Potassium *tert*-butoxide, tin tetrachloride, dichloroacetaldehyde diethyl acetal, 4,4′-biphenol, but-2-yne-1,4-diol, and 1,4-dichlorobut-2-yne were obtained from Aldrich Chemical Co. Hexabutyldistannoxane, boron tribromide, and dicobalt octacarbonyl were procured from Alfa Products, Ventron Division. Compounds **3**, **11**, **28**, 1,2,3,4,6-penta-*O*-acetyl-α-D-mannopyranose, 1,2,3,4,6-penta-*O*-acetyl-D-galactopyranose, and 1,2,3,4-tetra-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranose (gentibiose octaacetate) were obtained from Sigma Chemical Co. All commercial samples were employed without further purification. Compounds **9** and **13** were prepared by literature methods.[18,19] Methylene chloride and 1,2-dichloroethane were dried by distillation from phosphorus pentaoxide; methanol was distilled from magnesium methylate and stored under nitrogen; dioxane was distilled from calcium hydride. All reactions were performed under an atmosphere of nitrogen. Standard workup refers to pouring the reaction mixture into water, extracting the organic soluble material with methylene chloride, washing the combined extracts with water, drying the organic extracts over anhydrous $MgSO_4$, and concentrating the dried methylene chloride solution in vacuo under water-aspirator pressure (12–20 mm).

Preparation of Propynyl Glycosides 4, 6, 7, and 8. These compounds were prepared by the following general procedure. A solution of the appropriate peracetate (y mmol) in $ClCH_2CH_2Cl$ (1.6 y mL) was treated with $SnCl_4$ (y mmol). After 10 min, 2-propynol (1.5 y mmol) was added and after 4 h at room temperature the reaction mixture was quenched into 5% aqueous $NaHCO_3$ (1.6 y L). Standard workup gave the crude product, which was further purified by crystallization or chromatography.

1,2,3,4,6-Penta-*O*-acetyl-β-D-glucopyranoside (**3**; 130 g, 333 mmol) gave **4** (70 g, 56%): mp 114–116 °C (lit.[20] 118–119 °C); $[\alpha]^{24}_D$ −37.4° (lit.[20] −50.5°); ^1H NMR δ 5.40–4.70 (m, 4 H), 4.40 (d, 2 H, J = 2.5 Hz), 4.30–4.10 (m 2 H), 3.90–3.50 (m, 1 H), 2.50 (t, 1 H, J = 2.5 Hz), 2.20–1.90 (os, 12 H).

1,2,3,4,6-Penta-*O*-acetyl-α-D-mannopyranose (21.5 g, 55 mmol) gave **6** (12.2 g, 58%): mp 102–105 °C (EtOH); ^1H NMR δ 4.40–3.80 (m, 5 H, with d at 4.30, J = 2 Hz), 2.53 (t, 1 H, J = 2 Hz), 2.17 (s, 3 H), 2.10 (s, 3 H), 2.03 (s, 3 H), 1.97 (s, 3 H).

Anal. Calcd for $C_{17}H_{22}O_{10}$: C, 52.83; H, 5.74. Found: C, 53.15; H, 5.93.

1,2,3,4,6-Penta-*O*-acetyl-D-galactopyranose (50 g, 130 mmol) gave **7** (22 g, 44%) as a mixture of isomers (α/β, 3:7): $[\alpha]_D$ +21.2°; ^1H NMR δ 5.60–4.93 (m, 3 H), 4.83 (d, 1 H, J = 7 Hz), 4.50–3.85 (m, 5 H with d at 4.35, J = 2 Hz), 2.50 (t, 1 H, J = 2 Hz), 2.30–1.90 (os, 12 H).

Anal. Calcd for $C_{17}H_{22}O_{10}$: C, 52.83; H, 5.74. Found: C, 52.54; H, 5.86.

Gentiobiose octaacetate (19 g, 28 mmol) gave **8** (4.0 g, 21%): mp 161–162 °C; $[\alpha]_D$ −33°; ^1H NMR δ 5.40–4.10 (m, 12 H, with d at 4.4, J = 2 Hz), 4.00–3.50 (m, 4 H), 2.50 (t, 1 H, J = 2 Hz), 2.20–1.83 (os, 21 H).

Anal. Calcd for $C_{29}H_{38}O_{18}$: C, 51.61; H, 5.68. Found: C, 51.94; H, 5.89.

Stannate Method[21] for the Preparation of Glycosides 29 and 37. The following procedure was adopted. A solution of but-2-yne-1,4-diol (11 g, 128 mmol) and hexabutyldistannoxane (80 g, 134 mmol) in toluene (200 mL) was heated to reflux and the water formed removed azeotropically with a Dean–Stark tube. After 6 h, the reaction mixture was concentrated in vacuo to a mobile brown oil. Further heating at 100 °C under reduced pressure (0.1 mm), to remove all volatiles, gave 85 g (128 mmol, 100%) of the bis(tributylstannoxane). This material was used directly in the next step without further purification. To an ice-cold solution of **28** (110 g, 267 mmol) in CH_2Cl_2 (400 mL) was added (5 min) $SnCl_4$ (66.8 g, 256 mmol). After 10 min, a solution of the bis(tributylstannoxane) in CH_2Cl_2 (100 mL) was added over a period of 5 min. As the reaction progressed, a thick gelatinous precipitate was obtained, which slowly dissolved at the end of 4 h. After 7 h the reaction mixture was quenched into a vigorously stirred saturated aqueous $NaHCO_3$ solution (1 L). After being stirred for an additional 10 min, the thick slurry was suction filtered through a coarse glass frit. The filtrate was then transferred to a separatory funnel and the organic layer separated. The aqueous layer was extracted with $CHCl_3$ (2 × 200 mL) and the combined organic fraction dried, filtered, and concentrated in vacuo to a pale-green oil. The product **29** (R_f 0.20) was obtained as a pinkish-white solid upon chromatographic purification (solvent B, 1:4). Crystallization from a EtOH–C_6H_{12} (3 times) mixture gave **29** (16 g, 17%): mp 119–122 °C (EtOH); $[\alpha]^{24}_D$ −47.3°; ^1H NMR δ 5.66–4.70 (m, 8 H), 4.30–3.80 (m, 6 H), 3.40 (s, 4 H), 2.20–1.90 (os, 24 H).

Anal. Calcd for $C_{32}H_{42}O_{20}$: C, 51.45; H, 5.67. Found: C, 51.14; H, 5.51.

Reaction of **28** (25 g, 61 mmol) with the bis(tributylstannoxane) of **36** (24 g, 30 mmol) gave **37** (3.9 g, 15%): mp 209–212 °C; $[\alpha]_D$ −12,3°; ^1H NMR δ 7.55–7.30 (m, 2 H), 7.10–6.80 (m, 2 H), 5.40–4.85 (m, 4 H), 4.35–3.63 (m, 3 H), 2.15–1.85 (m, 12 H).

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Anal. Calcd for $C_{42}H_{46}O_{20}$: C, 57.91; H, 5.33. Found: C, 57.62; H, 5.58.

Preparation of Propynyl Sugars 10 and 12. These were prepared by the phase-transfer-catalyzed alkylation of the appropriate sugar precursor (y mmol) with 2-propynyl bromide (y mmol), using 50% aqueous NaOH (1.25 y L) and CH_2Cl_2 (2.5 y L) as the two phases, and benzyltriethylammonium bromide (0.5 y mmol) as the phase-transfer catalyst. The reaction was monitored by TLC and upon completion (3–4 h) was worked up in the usual manner.

3,5-*O*-Benzylidene-1,2-*O*-isopropylidene-α-D-glucofuranose (**9**; 10 g, 32 mmol) gave 8.7 g (78%) **10**: mp 76–78 °C; $[\alpha]^{22}_D$ +4.86° (c 3, $CHCl_3$); ^1H NMR δ 7.67–7.17 (m, 5 H), 6.07 (d, 1 H, J = 4 Hz), 6.0 (s, 1 H), 4.70 (d, 1 H, J = 4 Hz), 4.65–4.35 (m, 2 H), 4.30 (d, 1 H, J = 2 Hz), 4.10–3.90 (m, 2 H), 2.50 (t, 1 H, J = 2 Hz), 1.60 (s, 3 H), 1.37 (s, 3 H).

Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: 65.71; H, 6.43.

1,2:5,6-Diisopropylidene-α-D-glucofuranose (**11**; 26 g, 100 mmol) gave 27 g (87%) **12** as a syrup: n^{25}_D 1.461; $[\alpha]_D$ −15°; ^1H NMR δ 5.85 (d, 1 H, J = 4.0 Hz), 4.67 (d, 1 H, J = 4.0 Hz), 4.30 (d, 1 H, J = 2.0 Hz), 4.30–3.90 (m, 5 H), 2.50 (t, 1 H, J = 2.0 Hz), 1.55 (s, 3 H), 1.48 (s, 3 H), 1.42 (s, 3 H), 1.37 (s, 3 H).

Anal. Calcd for $C_{15}H_{22}O_6 \cdot 0.5H_2O$: C, 59.43; H, 7.26. Found: C, 59.28; H, 7.34.

2-Propynyl 2,3,4,6-Tetra-*O*-methyl-β-D-glucopyranoside (15). A solution of **4** (25 g, 65 mmol) and methyl iodide (80 mL) in DMF (300 mL), contained in a three-neck, round-bottom flask equipped with a mechanical stirrer, was cooled to −8 °C by means of an ice–salt bath. To this vigorously stirred solution was added in succession dibenzo-18-crown-6 (0.25 g, 0.70 mmol), powdered BaO (125 g, 82 mmol), and powdered $Ba(OH)_2 \cdot 8H_2O$ (50 g, 158 mmol). A slight exotherm was noticed and the reaction temperature rose to 5 °C before it dropped back down to −8 °C. The reaction mixture was slowly warmed to room temperature and, after a further 16 h at this temperature, the thick white gelatinous mixture was poured into water (300 mL). The undissolved barium salts were removed by filtration and the filtrate continuously extracted with a mixture of ether–hexane (1:9, v/v) for a period of 24 h. Concentration of the extracts in vacuo gave a pale-yellow oil, which was vacuum distilled to give **15** (13.5 g, 76%) as a pale-green liquid, which solidified on standing: bp 100 °C (0.035 mm); mp 40–45 °C; $[\alpha]_D$ −63.6°; ^1H NMR δ 4.50 (d, 1 H, J = 7 Hz); 4.43 (d, 1 H, J = 2 Hz), 3.80–2.87 (m, 18 H, os at 3.67, 3.60, 3.53, 3.43), 2.50 (t, 1 H, J = 2 Hz).

Anal. Calcd for $C_{13}H_{22}O_6$: C, 56.90; H, 8.02. Found: C, 56.84; H, 7.90.

Preparation of *S*-Propynyl Glycosides 14 and 31. A solution of **13** (3.64 g, 10 mmol) in acetone (10 mL) was treated with aqueous K_2CO_3 (1.4 g/10 mL) for a period of 5 min. 2-Propynyl chloride (0.85 g, 12 mmol) was then added, and the mixture was stirred for an hour and then poured into ice water. The precipitated product **14** was collected, washed with water, and crystallized three times from a ether–petroleum ether mixture: yield 3.3 g (82%); mp 70–72 °C; $[\alpha]_D$ −75.6°; ^1H NMR δ 5.40–4.66 (m, 4 H), 4.30–4.15 (m, 2 H), 4.00–3.60 (m, 1 H), 3.60–3.40 (m, 2 H), 2.30 (t, 1 H, J = 2 Hz), 2.15–1.90 (os, 12 H).

Anal. Calcd for $C_{17}H_{22}O_9S_1 \cdot 0.25H_2O$: C, 50.16; H, 5.58; S, 7.87. Found: C, 50.28; H, 5.67; S, 7.57.

Reaction of **13** (18.2 g, 50 mmol) with 1,4-dichloro-2-butyne (3.2 g, 26 mmol) using the same procedure gave **31** (18.0 g, 92%): mp 157–160 °C (EtOH–$CHCl_3$); $[\alpha]_D$ −109.5°; ^1H NMR δ 5.50–4.50 (m, 8 H), 4.37–4.10 (m, 4 H), 3.93–3.53 (m, 2 H), 3.53–3.37 (m, 4 H), 2.17–1.83 (os, 24 H).

Anal. Calcd for $C_{32}H_{42}O_{18}S_2$: C, 49.34; H, 5.44; S, 8.22. Found: C, 49.33; H, 5.30; S, 7.87.

1,1′-(2,2-Dichloroethylidene)bis[4-methoxybenzene] (34). Anisole (**33**; 21.63 g, 200 mmol) and dichloroacetaldehyde diethyl acetal (18.70 g, 100 mmol) were dissolved in glacial acetic acid (40 mL), and the solution was cooled in an ice–water bath (5 °C). Concentrated H_2SO_4 (30 mL) was then slowly (30 min) added with good stirring being maintained throughout the addition. After 2 h the thick slurry obtained was poured into ice water (400 mL) and the precipitated product collected by suction filtration. Crystallization from EtOH–$CHCl_3$ gave the pure product: 20.7 g (67%); mp 114–116.5 °C (lit.[22] 113 °C); ^1H NMR δ 7.40–7.05 (m, 4 H), 6.97–6.70 (m, 4 H), 6.27 (d, 1 H, J = 8 Hz), 4.50 (d, 1 H, J = 8 Hz), 3.70 (s, 6 H).

1,1′-(1,2-Ethynediyl)bis[4-methoxybenzene] (35). A powdered mixture of **34** (60.5 g, 195 mmol) and potassium *tert*-butoxide (100 g, 890 mmol) was slowly heated to 195 °C with an oil bath. At 120 °C a vigorous reaction ensued with the bulk of the *tert*-butyl alcohol being distilled off, leaving a brown-yellow cake. After 2 h at 195 °C the reaction mixture was cooled and the solid melt quenched into ice water (400 mL). The product was collected by filtration, washed with cold water, and then crystallized from EtOH–$CHCl_3$ to give **35** (30.5 g, 66%): mp 144–146 °C (lit.[23] 144–145 °C); ^1H NMR δ 7.60–7.27 (m, 4 H), 7.00–6.70 (m, 4 H), 3.77 (s, 6 H).

1,1′-(1,2-Ethynediyl)bis[4-hydroxybenzene] (36). A solution of **35** (13.5 g, 56 mmol) in CH_2Cl_2 (150 mL) was cooled to −78 °C (dry ice–acetone bath) and treated dropwise (45 min) with a solution of BBr_3 (25 g, 100 mmol) in CH_2Cl_2 (50 mL). The deep-purple solution thus obtained solidified on keeping overnight. This solid mixture was quenched into ice–water (500 mL) and the suspended solid dissolved in ether (200 mL). The aqueous layer was extracted with ether (2 × 150 mL) and the combined ether fraction extracted with 2 N NaOH (2 × 250 mL). The basic solution was then neutralized to pH 1 with concentrated HCl and subsequently extracted with ether (3 × 150 mL). Usual processing of these extracts gave a red-brown solid, which was recrystallized (4 times) from aqueous EtOH to give **36** (7.6 g, 64%) as a brown solid: mp 198–207 °C (lit.[23] 204–209 °C); ^1H NMR (CD_3COCD_3) δ 9.00–7.70 (br s, 2 H, OH), 7.65–7.27 (m, 4 H), 7.10–6.70 (m, 4 H).

Cyclotrimerization of Acetylenic Sugars. The following general procedure was adopted. A solution of the appropriate acetylenic precursor (y mmol) in dry dioxane (y mL) was brought to reflux. After 5 min, dicobalt octacarbonyl (5 mol %) was added and the reaction mixture maintained at reflux until the reaction had run to completion (TLC analysis). Workup was effected by concentration in vacuo followed by chromatographic purification on silica gel. Details such as reaction time, chromatography (chr) solvent, R_f, and crystallization solvent are given below.

Cyclotrimerization of 4 (25 g, 65 mmol): reaction time 4.6 days; chr solvent B (7:11); R_f 0.11; recrystallization (3 times) from EtOAc–C_6H_{12} gave **5a** (11 g, 44%); mp 144.5–147.5 °C $[\alpha]_D$ −60.6°; ^1H NMR δ 7.40–7.26 (m, 3 H), 5.40–4.40 (m, 18 H), 4.40–4.17 (m, 6 H), 3.90–3.50 (m, 3 H), 2.20–1.85 (os, 36 H); ^{13}C NMR δ 170.16, 169.74, 168.98, 168.81, 136.58, 134.77, 134.47, 128.49, 127.79, 127.09, 99.31 (C_1, d, J = 162.2 Hz), 72.60, 71.66, 71.19, 70.14, 68.20, 61.70, 20.51.

Anal. Calcd for $C_{51}H_{66}O_{30}$: C, 52.83; H, 5.74. Found: C, 52.83; H, 5.75.

Cyclotrimerization of 6 (10 g, 26 mmol): reaction time 21 days; reaction solvent xylenes (bp 140–144 °C); chr solvent D (35:64:1); R_f 0.24; trituration with EtOH gave **16** (3 g, 30%) as a brown foam; $[\alpha]_D$ +77.8°; ^1H NMR δ 7.43–7.20 (m, 3 H), 5.53–3.80 (m, 27 H), 2.30–1.90 (os, 36 H); ^{13}C NMR δ 170.51, 169.86, 169.75, 169.66, 137.16, 136.84 (1,3,5 isomer), 135.11, 134.88, 130.08, 129.35, 128.18, 127.48 (1,3,5 isomer), 96.79 and 96.61 (C_1, d, J = 171.1 Hz), 69.47, 69.09, 68.86, 67.37, 66.93, 66.11, 62.39, 20.83 (q), 20.74 (q), 20.65 (q).

Anal. Calcd for $C_{51}H_{66}O_{30}$: C, 52.83; H, 5.74. Found: C, 53.05; H, 6.01.

Cyclotrimerization of 7 (17 g, 44 mmol): chr solvent D (34.5:64.5:1); R_f 0.33; trituration from EtOH–C_6H_{12} gave **17** (7.0 g, 41%) as a pale-yellow foam: ^1H NMR 7.30–7.20 (m, 3 H), 5.50–3.80 (m, 27 H), 2.30–1.83 (m, 36 H); ^{13}C NMR δ 170.30, 170.16, 170.01, 169.22, 136.93, 134.97, 128.85, 128.21, 127.51, 99.95 (β isomer), 95.10 (α isomer), 70.76, 68.89, 67.98, 67.48, 67.07, 66.58, 61.54, 61.22, 20.62 (q).

Anal. Calcd for $C_{51}H_{66}O_{30} \cdot 0.5C_7H_8$ (toluene): C, 54.29; H, 5.86. Found: C, 53.94; H, 5.98.

Cyclotrimerization of 8 (2.8 g, 4 mmol): reaction time 4.2 days; chr solvent B (35:65); R_f 0.08; crystallization from EtOH gave semicrystalline **18** (1.7 g, 61%); mp 192–202 °C; $[\alpha]_D$ −49.2°; ^1H NMR δ 7.30 (br s, 3 H), 5.40–3.40 (m, 48 H), 2.20–1.70 (os,

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63 H); ^{13}C NMR δ 170.48, 170.21, 170.07, 169.48, 169.34, 169.28, 169.22, 169.13, 137.60 (1,3,5 isomer), 136.87, 135.23, 134.56, 128.62, 127.48, 127.24, 126.10 (1,3,5 iosomer), 100.74 (d, J = 163.8), 99.40 (d, J = 161.6 Hz), 72.75, 71.93, 71.29, 71.02, 70.17, 69.12, 68.71, 68.30, 61.84, 20.68 (q), 20.56 (q).

Anal. Calcd for $C_{87}H_{114}O_{54}$: C, 51.61; H, 5.68. Found: C, 51.32; H, 5.78.

Cyclotrimerization of 10 (21.45 g, 62 mmol): reaction time 7 days; chr solvent B (15:85); R_f 0.20; trituration from a EtOH–C_6H_{12} mixture gave **19** (10.05 g, 47%) as a foam; $[\alpha]_D$ +1.8°; ^{1}H NMR δ 7.70–7.10 (m, 18 H), 6.13–5.80 (m, 6 H), 4.80–4.10 (m, 18 H), 4.00–3.55 (m, 6 H), 1.53 (s, 9 H), 1.33 (s, 9 H); ^{13}C NMR δ 138.47, 137.95, 137.83, 137.66, 135.79, 135.37, 128.94, 128.18, 127.19, 126.07, 111.62 [$(CH_3)_2C(-O)$], 104.84 (ddd, J = 182.8, 5.1, 4.4 Hz; benzylidene C), 95.12 (d, 164.6 Hz), 83.89 (d, J = 160.9 Hz), 78.10, 73.30, 73.07, 72.60, 71.55, 71.31, 71.08, 70.85, 26.74 (q), 26.03 (q).

Anal. Calcd for $C_{57}H_{66}O_{18}$·0.25C_7H_8 (toluene): C, 66.41, H, 6.46. Found: C, 66.40; H, 6.72.

Cyclotrimerization of 12 (20 g, 67 mmol): reaction solvent xylenes (bp 137–144 °C); chr solvent B (20:80); R_f 0.18; trituration from ether–petroleum ether gave **20** (3.8 g, 20%); $[\alpha]_D$ −36.2°; ^{1}H NMR δ 7.40–7.25 (m, 3 H), 5.9 (d, 3 H, J = 4 Hz), 4.93–3.90 (m, 24 H), 1.50 (s, 9 H), 1.43 (s, 9 H), 1.38 (s, 9 H), 1.33 (s, 9 H); ^{13}C NMR δ 138.27 (1,3,5 isomer), 137.74, 136.14, 135.55, 129.50, 128.33, 127.24, 125.93 (1,3,5 isomer), 111.77, 109.14, 109.0, 105.25, 83.02, 82.66, 82.31, 81.79, 81.67, 81.26, 72.51, 72.25, 71.93, 69.79, 69.53, 67.45, 67.40, 26.82 (q), 26.27 (q), 25.86 (q), 25.42 (q).

Anal. Calcd for $C_{45}H_{66}O_{18}$·3/2H_2O: C, 58.60, H, 7.55. Found: C, 58.60; H, 7.41.

Cyclotrimerization of 14 (10 g, 25 mmol): reaction time 5 days; chr using solvent D (34.5:64.5:1) gave unreacted **14** (2.1 g) and **21** (R_f 0.21, 1.25 g, 16% based on recovered **14**); $[\alpha]_D$ −105.7°; ^{1}H NMR δ 7.23–7.10 (m, 3 H), 5.30–4.73 (m, 9 H), 4.50–3.33 (m, 18 H), 2.20–1.83 (os, 36 H); ^{13}C NMR δ 170.48, 170.04, 169.31, 137.72 (1,3,5 isomer), 136.60, 135.61, 134.41, 131.60, 131.16, 128.82 (1,3,5 isomer), 128.38, 82.11, 81.90, 75.85, 75.73, 73.74, 69.82, 69.71, 68.30, 62.10, 32.94, 30.66, 30.39, 20.77 (q), 20.62 (q), 20.53 (q).

Anal. Calcd for $C_{51}H_{66}O_{27}S_3$·H_2O: C, 49.98, H, 5.60; S, 7.83. Found: C, 49.85; H, 5.42; S, 7.41.

Cyclotrimerization of 15 (10 g, 36 mmol): reaction time 4.8 days; chr using solvent C (29:69:2) gave unreacted **15** (R_f 0.60, 1.2 g) and **22** (R_f 0.20, 3.6 g) as a pale-yellow solid. Trituration from ether–petroleum ether gave the pure product **22** (3.1 g, 41%) as a white solid: mp 116–35 °C; $[\alpha]_D$ −65.3 (c 2.9, $CHCl_3$); 7.45–7.20 (m, 3 H), 5.10–4.00 (m, 9 H), 3.70–2.90 (m, 42 H); ^{13}C NMR δ 137.89, 137.25 (1,3,5 isomer), 135.64, 135.11, 128.94, 128.33, 127.13, 126.45 (1,3,5 isomer), 102.38, 100.11, 86.58, 86.47, 83.83, 79.42, 74.68, 71.37, 70.67 (benzyl C, 1,3,5 isomer), 70.55, 68.36, 68.07, 60.73, 60.49, 60.29, 59.32.

Anal. Calcd for $C_{39}H_{66}O_{18}$: C, 56.90; H, 8.02. Found: C, 57.12; H, 7.91.

Cyclotrimerization of 29 (16 g, 41.4 mmol): reaction time 17 h; Product (R_f 0.14) isolated by chr using solvent E (1:65) as eluant. Recrystallization (5 times) from EtOH gave **30a** (15.2 g, 95%): mp 101–111 °C; $[\alpha]_D$ −41.5°; ^{1}H NMR δ 5.50–3.60 (m, 54 H), 2.30–1.80 (os, 72 H); ^{13}C NMR δ 170.27, 169.74, 169.04, 168.81, 137.23, 99.43 (C_1, d, J = 161.5 Hz), 72.60, 71.78, 71.31, 68.14, 63.87, 61.52, 20.57.

Anal. Calcd for $C_{96}H_{126}O_{60}$: C, 51.45; H, 5.67. Found: C, 51.14; H, 5.85.

Cyclotrimerization of 31 (14 g, 34.8 mmol): reaction time 20 days; cobalt catalyst (1.3 g, 10 mol %); reaction worked up by pouring into concentrated HCl and then extracting with $CHCl_3$. Purification by chr (2) using CH_3OH–toluene (1:65) as eluant gave **32** (R_f 0.10) as a brown foam (4.0 g, 29%); $[\alpha]_D$ −66.5°; ^{1}H NMR δ 5.40–3.33 (m, 54 H), 2.33–1.63 (os, 72 H); ^{13}C NMR δ 170.62, 169.98, 169.39, 135.73, 82.55 (d, J = 154.3 Hz), 75.97, 75.82, 73.68, 70.14, 68.45, 62.33, 27.82, 20.86, 20.77, 20.56.

Anal. Calcd for $C_{96}H_{126}O_{54}S_6$: C, 49.34; H, 5.44; S, 8.22. Found: C, 49.51; H, 5.22; S, 8.26.

Cyclotrimerization of 37 (2.75 g, 3.3 mmol): reaction time 3 days; product (R_f 0.11) isolated by chr using solvent D (34:64:2) as eluant. Crystallization from EtOH–$CHCl_3$ gave **38** (1.1 g, 40%); mp 311–315 dec °C; $[\alpha]_D$ +208.9°; ^{1}H NMR δ 6.38–6.30 (m, 24 H), 5.40–4.80 (m, 24 H), 4.50–3.50 (m, 18 H), 2.20–1.65 (os, 72 H); ^{13}C NMR δ 170.42, 170.01, 169.37, 154.51 (s), 139.94 (s), 135.37 (s), 132.27 (d, J = 166.8 Hz), 115.43 (d, J = 162.3 Hz), 99.0 (d, J = 164.5 Hz), 72.54, 71.90, 71.20, 68.21, 61.84, 20.59 (q, J = 129 Hz).

Anal. Calcd for $C_{126}H_{138}O_{60}$: C, 57.91; H, 5.33. Found: C, 57.61; H, 5.54.

Preparation of Deacetylated Glycosides 5b and 30b. The following general procedure was adopted. The acetylated glycoside (y mmol) was slurried in CH_3OH (12 y mL) and treated with sodium (0.05 y mmol). After 16 h, the reaction mixture was neutralized with Dowex 50W(H^+) ion-exchange resin (0.1 y mmol), filtered, and concentrated in vacuo to give the product.

Compound **5a** (5.65 g, 4.88 mmol) gave **5b** (2.9 g, 91%): mp 140–150 °C; $[\alpha]_D$ −72.0° (c 2, H_2O); ^{1}H NMR (D_2O) δ 7.60–7.40 (m, 3 H), 5.10–4.80 (m, 6 H, benzyl H), 4.67 (s, 12 H, HOD), 4.50 (d, 3 H, J = 7 Hz), 4.00–3.20 (m, 18 H).

Anal. Calcd for $C_{27}H_{42}O_{18}$·CH_3OH: C, 48.95; H, 6.76. Found: C, 49.18; H, 6.98.

Compound **30a** (8.0 g, 3.6 mmol) gave **30b** (4.2 g, 96%): $[\alpha]_D$ −72° (c 2, H_2O); ^{1}H NMR (D_2O) δ 5.60–5.00 (m, 12 H), 4.73 (s, 24 H, HOD), 4.50 (br d, 6 H, J = 7 Hz), 4.10–3.20 (m, 36 H); ^{13}C NMR (D_2O) δ 140.61, 103.50, 78.58, 78.29, 75.56, 72.21, 66.70, 63.44, 56.98.

Anal. Calcd for $C_{48}H_{78}O_{36}$·3/2H_2O: C, 45.80; H, 6.49. Found: C, 45.95; H, 6.85.

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Registry No. **3**, 604-69-3; **4**, 34272-02-1; **5a**, 83476-62-4; **5b**, 83476-70-4; **6**, 83476-52-2; **6** (1,3,5-cyclotrimerized), 83476-72-6; **7**, 83540-91-4; **8**, 83476-53-3; **8** (1,3,5-cyclotrimerized), 83476-73-7; **9**, 74708-51-3; **10**, 83476-58-8; **11**, 582-52-5; **12**, 67441-18-3; **12** (1,3,5-cyclotrimerized), 83476-74-8; **13**, 19879-84-6; **14**, 83476-60-2; **14** (1,3,5-cyclotrimerized), 83486-37-7; **15**, 83476-59-9; **15** (1,3,5-cyclotrimerized), 83476-75-9; **16**, 83476-63-5; **17**, 83540-92-5; **18**, 83486-35-5; **19**, 83476-64-6; **20**, 83476-65-7; **21**, 83476-66-8; **22**, 83476-67-9; **28**, 572-09-8; **29**, 83476-54-4; **30a**, 83476-68-0; **30b**, 83476-71-5; **31**, 83476-61-3; **32**, 83476-69-1; **33**, 100-66-3; **34**, 7388-31-0; **35**, 2132-62-9; **36**, 22608-45-3; **36** bis(tributylstannoxane), 83476-57-7; **37**, 83476-55-5; **38**, 83486-36-6; dicobalt octacarbonyl, 10210-68-1; 2-propylnol, 107-19-7; 1,2,3,4,6-penta-*O*-acetyl-α-D-mannopyranose, 4163-65-9; 1,2,3,4,6-penta-*O*-acetyl-D-galactopyranose, 25878-60-8; gentiobiose octaacetate, 4613-78-9; but-2-yne-1,4-diol, 110-65-6; hexabutyldistannoxane, 56-35-9; bis(tributylstannoxane), 83476-56-6; 2-propynyl bromide, 106-96-7; 2-propynyl chloride, 624-65-7; 1,4-dichloro-2-butyne, 821-10-3; dichloroacetaldehyde diethyl acetal, 619-33-0.