formation of a higher aggregate possibly with a spiro-like $Ga_3As_6$ unit with two four-membered rings connected by one central Ga atom.

The $[Ga_2(AsSi\mathit{i}Pr_3)_4]^{2-}$ ion shows a structural relationship with the Zintl ion $[Ga_2As_4]^{6-}$, which is contained in the ternary phase $Cs_6Ga_2As_4$.[6] This anion also has the shape of a $Ga_2As_2$ four-membered ring with two further exocyclic As atoms bonded to the Ga atoms. The exocyclic As–Ga bonds of the $[Ga_2As_4]^{6-}$ ions are 234.3 pm long, which is much shorter than usual for As–Ga single bonds, and suggests multiple-bond character. Because of the particular coordination numbers and conditions in this solid-state Zintl phase a comparison with the bonding situation in **2** is impossible. However, the $[Ga_2(AsSi\mathit{i}Pr_3)_4]^{2-}$ ion in **2** can be seen as a silyl derivative of the $[Ga_2As_4]^{6-}$ ion. Thus, **2** can be regarded as the first example of a silylated binary Zintl anion. So far only silylated Zintl anions of phosphorus and $[As_7(SiMe_3)_3]$ have been reported.[14]

*Experimental Section*

**2**: A butyllithium solution (1.6 M; 3.55 mL, 5.68 mmol) was added to a solution of $H_2AsSi\mathit{i}Pr_3$ (0.66 g, 2.84 mmol)[15] in THF (5 mL) of at 0 °C. After stirring for 1 h, this solution was added to a −50 °C solution of $GaCl_3$ (0.25 g, 1.42 mmol; 99.99 %) in heptane (20 mL). The reaction mixture was allowed to warm to room temperature and then stirred for additional 24 h. The resulting red solution was filtered to remove the precipitated LiCl. Subsequently this solution was reduced to about 10 mL in vacuo. After two days large orange crystals of **2** formed. Yield: 0.37 g (34 %); elemental analysis (%) calcd for $C_{60}H_{132}As_4Ga_2Li_2O_6Si_4$ (1515.0): C 47.57, H 8.78; found: C 45.77, H 8.24; $^1$H NMR ([D$_6$]benzene): $\delta = 3.720$ (m, 12 H, $(CH_2CH_2)_2O$), 1.593 (m, 21 H, *i*Pr) 1.540 (m, 12 H, $(CH_2CH_2)_2O$), 1.449 pm (m, 21 H, *i*Pr); $^{13}$C{$^1$H} NMR ([D$_6$]benzene): $\delta = 68.7$ (s, $(CH_2CH_2)_2O$), 25.7 (s, $(CH_2CH_2)_2O$), 21.3 (s, $CH_3$), 20.5 (s, $CH_3$), 16.5 (s, *C*H), 15.6 pm (s, *C*H); $^{29}$Si{$^1$H} NMR ([D$_6$]benzene): $\delta = 26.7$ pm (br); UV/Vis (suspension in mineral oil): $\lambda_{max} = 410$ nm (sh), 270 nm.

ESI-FTMS: Mass spectra were taken in a Fourier-Transform Ion Cyclotron Resonance Mass Spectrometer (Bruker Daltonics, APEX II) equipped with an electrospray source (Analytica of Branford).

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[9] STOE-IPDS, Schneider-rotating anode, graphite monochromator, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; **2**: $a = 1124.8(2)$, $b = 2430.4(5)$, $c = 1487.1(3)$ pm, $\beta = 99.99(3)^\circ$, $V = 4003.8(14) \times 10^6$ pm$^3$; monoclinic, $P2_1/n$, $Z = 2$, $\rho_{calcd} = 1.146$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 2.408$ mm$^{-1}$, $T = 200$ K, $2\Theta_{max} = 46^\circ$; 19418 reflections measured, 5525 independenr reflections, ($R_{int} = 0.0414$), 4787 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against $F^2$, 290 parameters (As, Ga, Si, O, Li atoms refined aniosotropically, C atoms refined isotropically with split positions, the positions of H atoms where not determind), $R1 = 0.0620$, $wR2 = 0.1942$ (all data), residual electron density: 0.575 e Å$^{-3}$. CCDC-174606 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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## Total Synthesis of Woodrosin I**

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Plants belonging to the *Convovulacaeae* family are rich sources of alkaloids and resin glycosides. Although intriguingly complex in detail, the latter invariably contain (11*S*)-hydroxyhexadecanoic acid (jalapinolic acid) as a common aglycon, which is usually tied back to form a characteristic macrolide ring that spans two or more sugar units of their oligosaccharide backbones.[1] The biological functions and physiological properties of resin glycosides are far from fully understood; however, diverse and promising effects have been described for some of these compounds, for example,

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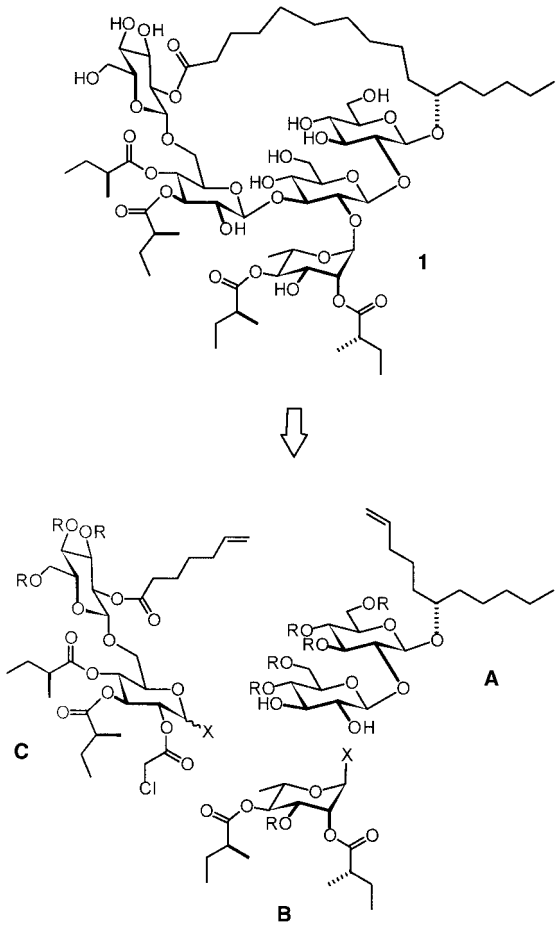
cytotoxicity against human cancer cell lines, hemolytic action, antibacterial activity, purgative properties, and significant plant growth regulating capacity.[1, 2] Only recently have preparative studies directed towards these challenging targets been reported in the literature which may help to map their structure – activity relationships in more detail.[2–4]

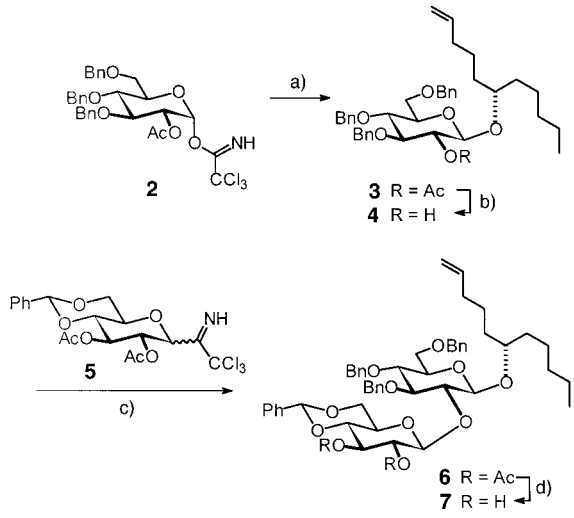
Herein, we describe the first total synthesis of woodrosin I (**1**) a glycolipid isolated from the stems of *Ipomoea tuberosa* L. (*Merremia tuberosa* (L.) Rendle). This plant is commonly called woodrose because of the shape of its dried calyx.[5] Compound **1** (Scheme 1) is one of the most complex resin glycosides known to date. Particularly challenging motifs are the lactone moiety spanning four glucose units to form a 27-membered macrocycle, the additional acylation pattern at the periphery, which seriously restricts the possible choice of temporary protecting groups, as well as the branching of the pentasaccharide perimeter at vicinal positions, which results in severe steric crowding in this region of the molecule.

Our previous experience with ring closing metathesis (RCM),[2a,b, 6, 7] encouraged us to synthesize the macrolide core of **1** by this method as well. To ensure maximum efficiency, the formation of stable chelates of the intermediate Lewis acidic metal carbene species with the polar substituents of the substrate must be avoided as such arrays seriously attenuate the activity of the catalysts used;[8, 9] this should be possible by targeting the C6–C7 bond within the aliphatic tether. Since the cycloalkene formed by RCM has to be hydrogenated anyway, benzyl ethers or benzylidene acetals are the clear choice for the residual protecting groups R, except for those positions where neighboring-group participation is needed to control the glycosylation reactions.




Scheme 1. Retrosynthetic analysis of woodrosin I (**1**).

The cyclization precursor itself can be assembled in a highly convergent manner from the disaccharide building blocks **A** and **C** and the rhamnosyl donor **B** (Scheme 1), which were obtained as described in Schemes 2 – 4. Specifically, the known trichloroacetimidate **2**[10, 11] was glycosylated with (6*S*)-undec-1-en-6-ol, which is available in excellent optical purity ($\geq$99 % *ee*) by an enantioselective addition of dipentylzinc to 5-hexenal.[2] Cleavage of the 2-O-acetyl group of **3** gave alcohol **4**, which was treated with the readily accessible trichloroacetimidate **5**[2] in the presence of catalytic amounts of $BF_3 \cdot Et_2O$ to give disaccharide **6** in 82 % yield. Subsequent deacetylation provided diol **7**, which corresponds to synthon **A** (Scheme 2).




Scheme 2. Synthesis of building block **A**. a) (6*S*)-Undec-1-en-6-ol, $BF_3 \cdot Et_2O$, $CH_2Cl_2$/hexane, –20 °C, 68 %; b) NaOMe (cat.), MeOH, quantitative; c) **5**, $BF_3 \cdot Et_2O$, $CH_2Cl_2$/hexane, –20 °C, 82 %; d) NaOMe (cat.), MeOH, 88 %.

Regioselective benzylation of allyl-L-rhamnoside **8**[12] by using established stannylation methodology[13] followed by DCC-mediated esterification of the resulting product **9** with commercially available (2*S*)-methylbutyric acid provided compound **10**, which was deprotected at the anomeric position on exposure to Pd/C in acidic MeOH (Scheme 3). The resulting hemiacetal **11** was converted under standard conditions[11] into imidate **12**, which serves as rhamnosyl donor **B** in the formation of the target.

The preparation of the third fragment started with 3,4,6-tri-*O*-benzyl-D-glucose (**14**), which was derived from glucal **13** (R = Bn, Scheme 4). Substrate **14** was esterified with 6-heptenoic acid in the presence of DCC and catalytic DMAP. Deprotection of the anomeric position with hydrazine acetate followed by treatment of the resulting hemiacetal with $Cl_3CCN$ and $Cs_2CO_3$ furnished glycosyl donor **15**. D-Glucal **13** (R = H) was also converted into the required glucosyl acceptor **17** by a sequence of routine manipulations. The $BF_3 \cdot Et_2O$-promoted glycosylation of imidate **15** with the 1,6-diol **17** proceeded with excellent selectivity, delivering compound **18**

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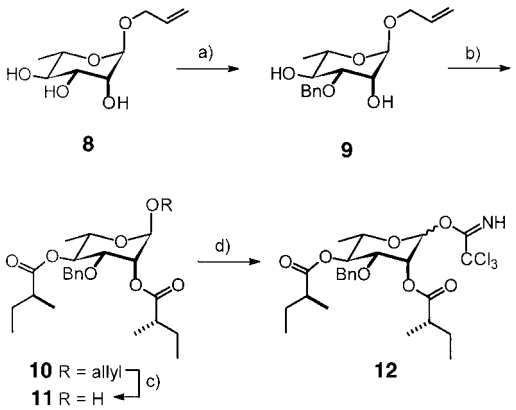
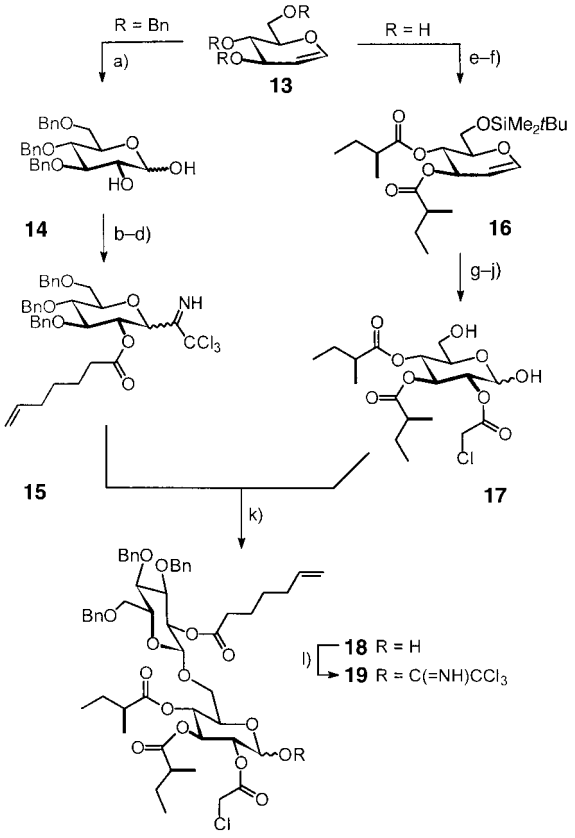


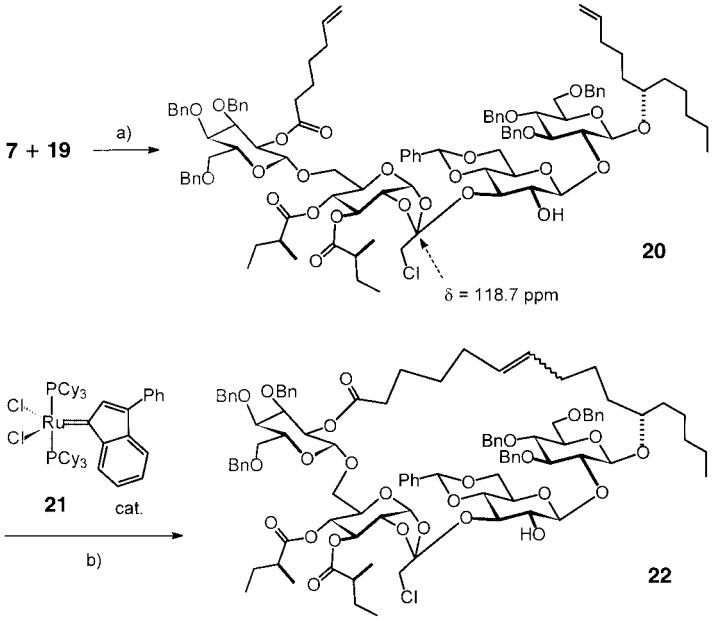

Scheme 3. Synthesis of building block **B**. a) 1) $Bu_2SnO$, toluene, reflux; 2) CsF, BnBr, DMF, 72%; b) (2*S*)-methylbutyric acid, DCC, DMAP, $CH_2Cl_2$, 89%; c) Pd/C, PPTS (cat.), MeOH, 80%; d) $Cl_3CCN$, $Cs_2CO_3$, $CH_2Cl_2$, 92%. DMF = *N*,*N*-dimethylformamide, DCC = *N*,*N*′-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine, PPTS = pyridinum *p*-toluenesulfonate.




Scheme 4. Synthesis of building block **C**. a) $OsO_4$ (cat.), NMO, acetone/$H_2O$, 94%; b) 6-heptenoic acid, DCC, DMAP (cat.), $CH_2Cl_2$, 99%; c) $H_2NNH_2 \cdot HOAc$, DMF, 83%; d) $Cl_3CCN$, $Cs_2CO_3$, $CH_2Cl_2$, 87%; e) *t*$BuMe_2SiCl$, imidazole, DMF, 70%; f) (2*S*)-methylbutyric acid, DCC, DMAP, $CH_2Cl_2$, 93%; g) $OsO_4$ (cat.), NMO, acetone/$H_2O$ (9:1), quantitative; h) chloroacetic acid anhydride, $Et_3N$, DMAP (cat.), $CH_2Cl_2$, $-20 \rightarrow -10\,^{\circ}C$, 83%; i) $BF_3 \cdot Et_2O$, $CHCl_3$, 81%; j) $H_2NNH_2 \cdot HOAc$, DMF, 79%; k) $BF_3 \cdot Et_2O$, $CH_2Cl_2$, $-20\,^{\circ}C$, 86%; l) $Cl_3CCN$, $Cs_2CO_3$, $CH_2Cl_2$, 54%. NMO = 4-methylmorpholine *N*-oxide.

in 86% yield. Because the anomeric position in this product was already unmasked, it was directly amenable to the preparation of the next glycosyl donor **19** (synthon **C**). This smooth reiterability of the trichloroacetimidate method is a largely unexplored feature and deserves further investigation.

The next stage of the synthesis required the efficient assembly of the individual building blocks to the pentasaccharide perimeter of woodrosin I. For steric reasons, however, this venture turned out to be far from trivial. Although it was possible to attach the rhamnose unit to the 2′-OH group of acceptor diol **7**, subsequent glycosylation of the resulting trisaccharide with donor **19** was invariably unsuccessful.[14] Therefore the alternative order for the glycosidation steps was explored. This option was facilitated by the distinctly different reactivity of the vicinal hydroxy groups in **7** which allowed consecutive glycosylation reactions without recourse to protecting groups. Thus, treatment of a mixture of **7** and **19** in $CH_2Cl_2$ at $-20\,^{\circ}C$ with a catalytic amount of TMSOTf afforded a single product in 84% yield. However, its NMR spectra (Bruker DMX 600) were inconsistent with the expected tetrasaccharide but corresponded to orthoester **20** formed by participation of the chloroacetyl moiety (Scheme 5). Most indicative is a singlet in the $^{13}C$ NMR spectrum at $\delta = 118.7$ ppm which corresponds to the newly formed orthoester junction.



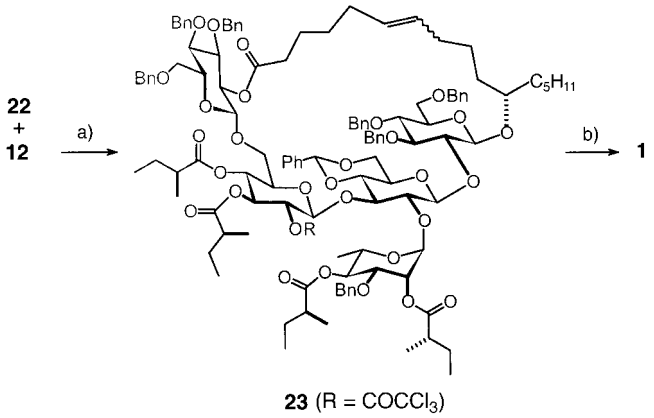

Scheme 5. Coupling of **7** and **19**, and RCM. a) TMSOTf (cat.), $CH_2Cl_2$, $-20\,^{\circ}C$, 84%; b) **21** (cat.), $CH_2Cl_2$, reflux, 94%. TMSOTf = trimethylsilyl trifluoromethanesulfonate.

The chloroacetyl group had originally been chosen because it would allow stereochemical control in the glycosidation reactions by neighboring group participation, but would still be orthogonal to the residual ester moieties in **1**. Despite some literature precedence for the engagement of chloroacetates in the formation of orthoesters, $\beta$-glycosides are usually obtained if the reactions are promoted with strong Lewis acids in the absence of a buffering base.[15, 16] Therefore the exclusive formation of **20** in the TMSOTf-catalyzed coupling of **7** and **19** was rather unexpected.

Irrespective of this outcome, the total synthesis of woodrosin I was pursued as it might be possible to rectify the connectivity pattern at a later stage. First, however, the severe steric hindrance in the vicinity of the orthoester moiety had to be overcome. Because the 2′-OH group of **20** is strongly shielded in this sector of the molecule, all attempts to attach the missing rhamnosyl unit to this innately unreactive site were in vain.[14] However, inspection of models suggested that the trajectory towards this hidden hydroxy group may be somewhat less narrow *after* forging the macrocyclic ring. Therefore the completion of the sugar backbone was postponed until after the RCM reaction.

Diene **20** cyclized in remarkably high yield to cycloalkene **22** on treatment with catalytic amounts of the indenylideneruthenium complex **21**.[17, 18] Catalyst **21** was introduced recently as a readily accessible and powerful substitute for the more popular Grubbs carbene [$(PCy_3)_2(Cl)_2Ru$=CHPh]. This favorable result highlights once more the truly remarkable utility of RCM even in complex cases.

With macrolide **22** in hand, the introduction of the missing rhamnose moiety was reinvestigated. In view of the lability of donor **12** in the presence of Lewis acids, an "inverse" glycosylation procedure was applied.[19] Thus, alcohol **22** was premixed with catalytic amounts of TMSOTf in rigorously dried $Et_2O$, and compound **12** was then added slowly to the resulting solution. The outcome of this key experiment surpassed our expectations (Scheme 6): not only was it




Scheme 6. Total synthesis: a) TMSOTf (cat.), $Et_2O$, 0 °C, slow addition of **12** (20 min), 30 min, 60 %; b) 1) $H_2NNH_2 \cdot HOAc$, DMF, $-10 \rightarrow 0$ °C, (ii) $H_2$ (1 atm), Pd/C, MeOH, 18 h, 84 % (over two steps).

possible to attach the missing rhamnose, but the compromising orthoester moiety of **22** was found to rearrange concomitantly to the required $\beta$-glycosidic linkage. After optimizing the premixing and addition times, product **23** was isolated in 60 % yield. In view of its selectivity, this transformation constitutes a hallmark for the power of the trichloroacetimidate method[11] and represents one of the most advanced applications of Kochetkov's orthoester protocol reported to date.[20]

Short treatment of product **23** with hydrazine acetate for the selective cleavage of the chloroacetyl group followed by extensive hydrogenation over Pd/C afforded fully deprotected woodrosin I (**1**). The spectral data (600 MHz) of this product are in excellent agreement with those reported in the literature.[5]

In summary, we have reported the first total synthesis of the complex resin glycoside woodrosin I (**1**). This venture not only showcases the relevance of RCM for natural product synthesis, but also attests to the maturity and flexibility of the trichloroacetimidate method pioneered by Schmidt et al.[11] Particularly promising yet largely unexplored aspects of the latter are the excellent selectivities observed in glycosylations of acceptors that contain more than one unprotected hydroxy group.[21]

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[14] Details will be reported separately in a full paper.

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