An Approach to *exo*-Enol Ether – Cyclic Ketal Structures Found in Marine Cembranoids, Based on Silver-Assisted Cyclisations of Enynone Precursors

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Abstract: Treatment of a solution of the (*E*)-enynone **17** in methanol with $AgNO_3$ leads to cyclisation and isolation of the substituted furan **25** in >95% yield, rather than the anticipated *exo*-enol ether–cyclic ketal structure **24**. By contrast, a similar Ag-mediated cyclisation of the related substituted enynone **20** led to the *exo*-enol ether–cyclic ketal structure **28** (50%) alongside the substituted furan **29** (45%). The outcomes of these silver-assisted enynone cyclisations are compared and contrasted with earlier studies with acid-catalysed reactions of furanoepoxides, for example **7**, which also lead to *exo*-enol ether–cyclic ketals, viz. **1**, and to substituted furanmethanol products, that is, **10**.

Key words: enols, enynes, acetals, cyclisation, natural products

The interesting and unusual *exo*-enol ether–cyclic ketal structural unit **1** is present in a number of cembranoid metabolites, for example **2**, **3**, and **4**, isolated from corals of the genus *Sinularia*.[1] In these corals the metabolites **2**–**4** are frequently found alongside furanmethanol and furanoepoxide – containing cembranoids, such as **5** and **6**, respectively (Figure 1).[2]

In earlier publications we have suggested that the structural unit **1** found in the metabolites **2**–**4**, most likely has its origin in furan-containing congeners akin to **5** and **6**, involving acid-catalysed displacement reactions of their oxy centres at C7 (cembranoid numbering) followed by quenching the furanoxonium ion intermediates produced in this manner with methanol (cf. structures **7**, **8**, and **9** in Scheme 1).[2] Using the epoxide **7** ($R^2 = R^3 = Me$) as a model, we indeed found that its treatment with PTSA–MeOH led to the enol ether–cyclic ketal **1** ($R^2 = R^3 = Me$). Unfortunately, however, the structure **1** was unstable and became rapidly isomerised under the reaction conditions to its furanmethanol methyl ether positional isomer **10** ($R^2 = R^3 = Me$, Scheme 1).[3]

In this paper, we have examined an alternative perspective on the relationship between the enol ether–cyclic ketal, furanmethanol, and furanoepoxide structural units in the metabolites **2**–**6**, surmising that the furanoxonium ion intermediate **9** in Scheme 1 could be formed instead from electrophilic activation of an acetylenic ketone precursor, viz. **13**.[4] This acetylenic ketone **13** is related to the vinyl carbocation species **14** and also to enedione compounds, viz. **12**, which can be produced in vivo by sequential oxi-

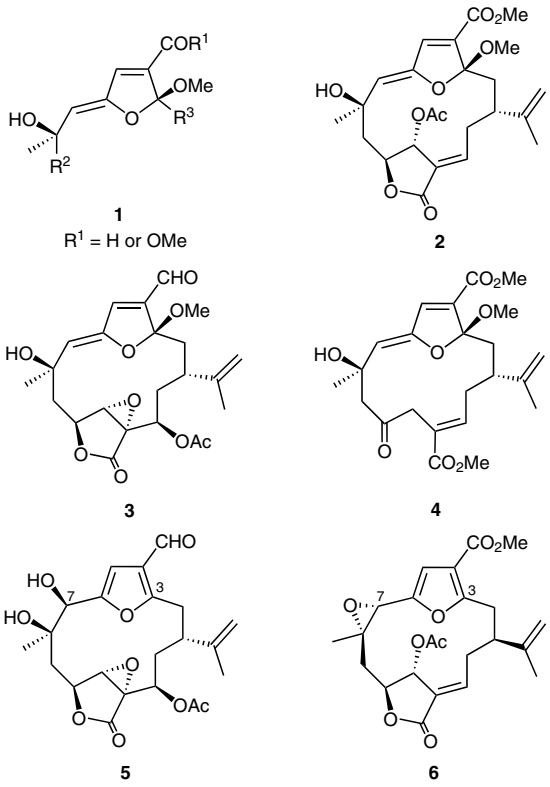
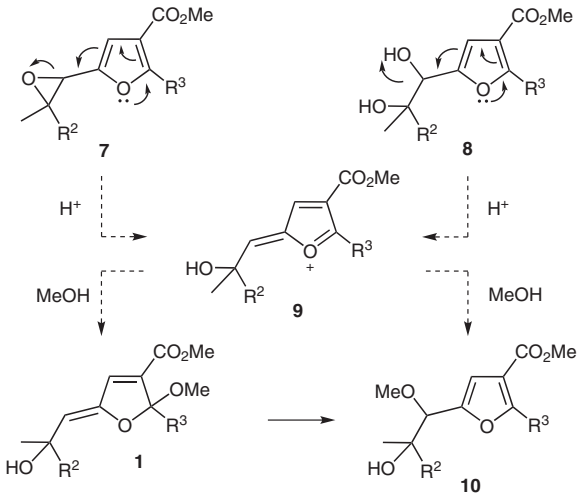


Figure 1 Structures of enol ether–cyclic ketal metabolites and their congeners in *Sinularia*



Scheme 1 Acid-catalyzed transformations of epoxyfurans to enol ether–cyclic ketals and furanmethanol derivatives

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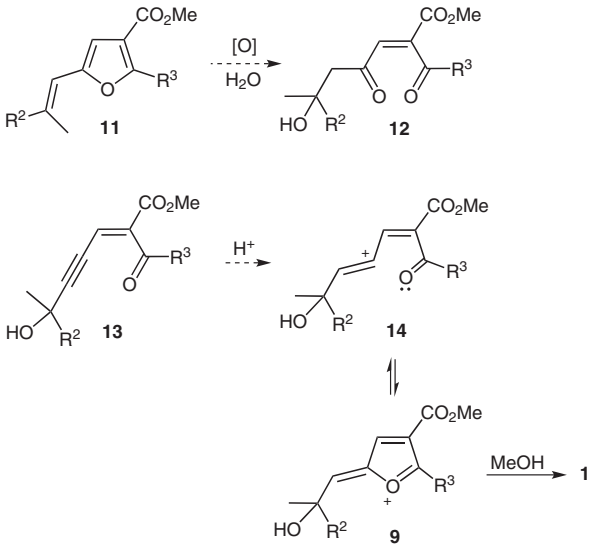
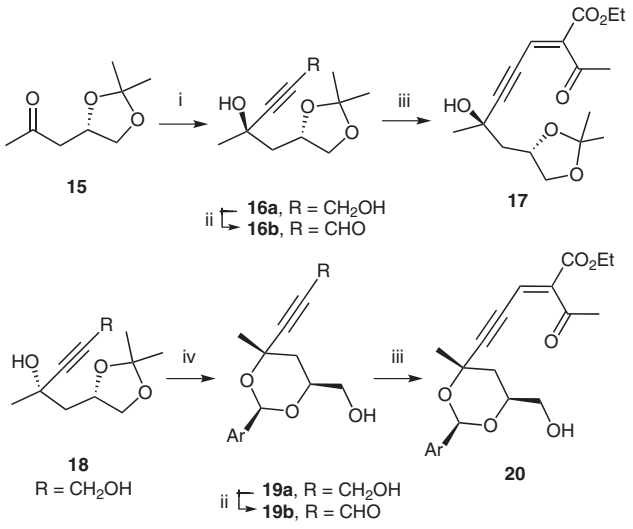


Scheme 2 Proposed mode of cyclisation of (*E*)-enynones to enol ether–cyclic ketals

dative cleavage and hydrolysis of alkenylfuran-containing precursors, that is, **11** (Scheme 2).[2]

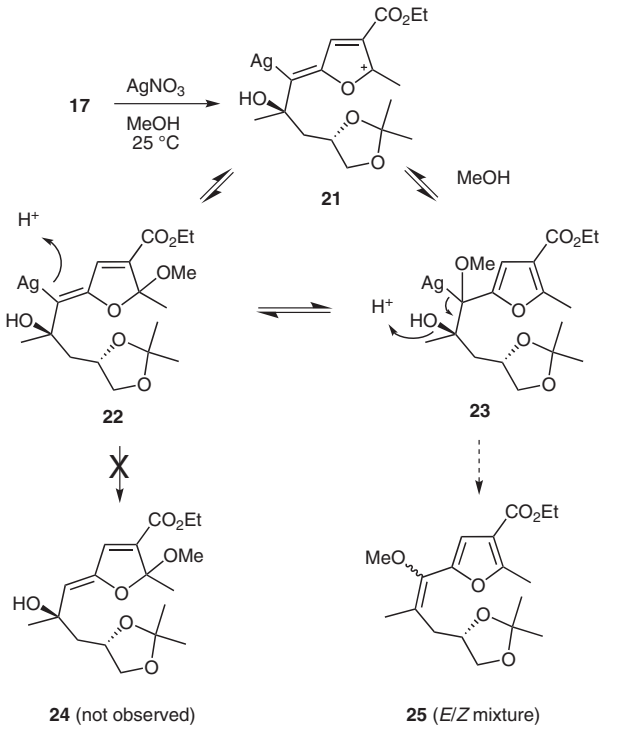
To examine the feasibility of the synthesis of *exo*-enol ether–cyclic ketals, viz. **1**, from electrophilic activation of acetylenic ketones of constitution **13**, we synthesised the substrates **17** and **20**. The substituted (*E*)-enynone **17** was smoothly prepared from the known methyl ketone **15**[5] following: i) addition of the bisanion of propargyl alcohol and separation of the diastereoisomer **16a** of the resulting *tert*-alcohol by chromatography; ii) oxidation of **16a** to the corresponding aldehyde **16b**, using MnO_2 in CH_2Cl_2,[6] and iii) a Knoevenagel condensation between **16b** and ethyl acetoacetate in the presence of piperidine–acetic acid, followed by separation of **17** from its *Z*-isomer formed concurrently by chromatography (Scheme 3).[6,7] The *p*-methoxy-benzylidene acetal **20**, corresponding to **17**, was synthesised starting from the diastereoisomer **18** of **16a**, which, by straightforward treatment with *p*-methoxybenzaldehyde dimethylacetal in the presence of camphorsulfonic acid, first gave **19a**. Oxidation of **19a** with MnO_2 and a Knoevenagel condensation of the resulting aldehyde **19b** with ethyl acetoacetate, followed by chromatography, then gave the benzylidene acetal substituted (*E*)-enynone **20**.[8]



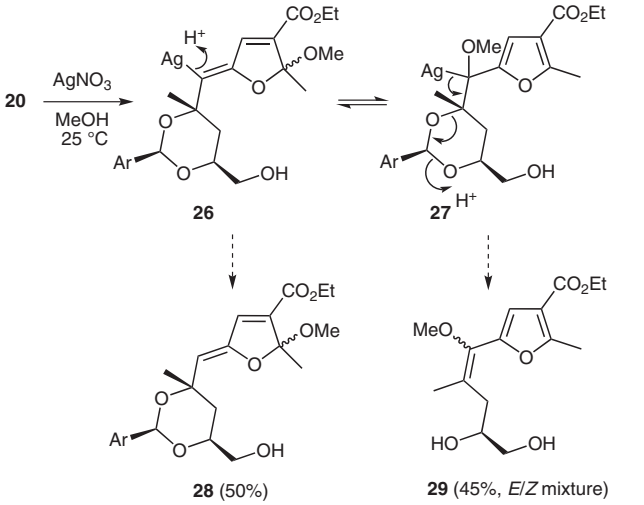
Scheme 3 Synthesis of the substituted (*E*)-enynones **17** and **20**. *Reagents and conditions*: i, $HOCH_2CCH$, BuLi, THF, –40 °C to r.t., 37% (**16a**) + 31% (**18**); ii, MnO_2, CH_2Cl_2, 25 °C, 69% (**16b**), 65% (**19b**); iii, $MeCOCH_2CO_2Et$, piperidine, AcOH, THF, 25 °C, chromatographic separation of *E*-isomers, 30% (**17**), 21% (**20**); iv, $ArCH(OMe)_2$, CSA, CH_2Cl_2, 0–25 °C, 78% (Ar = 4-$MeOC_6H_4$).

A number of electrophilic reagents have been used to activate acetylene-containing compounds as a prelude to their capture and cyclisation with proximal oxy functionalities.[9] We were attracted to examining the cyclisations of the (*E*)-enynone compounds **17** and **20** in the presence of Ag(I) in the form of silver nitrate. Thus, when a solution of the (*E*)-enynone **17** in dry methanol was stirred in the presence of anhydrous $AgNO_3$ for five minutes, work-up and chromatography gave a single cyclic product, containing an incorporated OMe substituent, in almost quantitative yield. The spectroscopic data for the new compound, however, were not consistent for those of the expected *exo*-enol ether–cyclic ketal product **24**. Instead, the spectroscopic data correlated with the furan structure **25** where the incorporated OMe substituent forms part of a different enol ether unit (Scheme 4).[10] The structure **25**, which was produced as a 3:2 mixture of *Z*- and *E*-isomers, is most likely derived from the enynone **17** via initial formation of the oxonium ion intermediate **21**. Addition of methanol to **21** would be expected to next lead to the equilibrating silver-bound intermediates **22** and **23**. Protonation of the sp^2 carbon-to-silver bond in **22** would then lead to the enol ether–cyclic ketal **24**, whereas protonation of the tertiary alcohol centre in **23** accompanied by elimination would give the substituted furan **25**. Presumably the elimination reaction from **23** is much faster than the protonation of **22**, which explains why the substituted furan **25** is produced exclusively and at the expense of **24**. In support of the foregoing proposal, treatment of the enynone **20** containing a benzylidene acetal unit at C7 (cf. **17**) with silver nitrate gave the anticipated *exo*-enol ether–cyclic ketal structure **28** alongside the furan structure **29** related to **25** (Scheme 5).[11] We presume that in this conversion, elimination from the silver-bound intermediate **27** (cf. **23**) producing **29** is retarded by the bulky benzylidene acetal substituent, thereby allowing the accumulation of the enol ether–cyclic ketal **28** from the equilibrating silver complex **26**. This rationale is also in accord with the observation that the cyclisation of **17** to **25** is complete within minutes, whereas the cyclisation of **20** to **28/29** takes more than 12 hours.

In conclusion, we have shown that solutions of appropriately functionalised (*E*)-enynones in methanol undergo cyclisation in the presence of $AgNO_3$ leading to enol ether–cyclic ketal structures, for example **28**, similar to those present in cembranoids metabolites isolated from corals, cf. **2**, **3**, and **4**.[4] This investigation therefore com-



Scheme 4 Rationalisation of the formation of the furan **25** from the (*E*)-enynone **17** in the presence of $AgNO_3$



Scheme 5 Formation of the *exo*-enol ether–cyclic ketal **28** from Ag(I)-assisted cyclisation of the (*E*)-enynone **20** (Ar = 4-$MeOC_6H_4$)

plements earlier work where the same *exo*-enol ether–cyclic ketal structures were derived from acid-catalysed reactions with furanoepoxides (Scheme 1).[1] However, these studies, taken together, highlight the sensitivity of the same *exo*-enol ether–cyclic ketal structures in vitro and their propensity for rearrangement and isomerisation to their more stable furan positional isomers, cf. structures **1** and **10**, **24** and **25**, also **28** and **29**.

Acknowledgment

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References and Notes

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(7) **Aldehyde 16b**
^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.35 [3 H, s, C*H*$_3$C(OR)$_2$CH$_3$], 1.41 [3H, s, CH$_3$C(OR)$_2$C*H*$_3$], 1.61 (3 H, s, C*H*$_3$COH), 1.96 [1 H, d(AB)d, *J* = 14.1, 5.5 Hz, CH(OR)C*H*HC], 2.15 [1 H, d(AB)d, *J* = 14.1, 7.2 Hz, CH(OR)CH*H*C], 3.47 [1 H,(br) s, OH], 3.64 (1 H, dd, *J* = 8.2, 7.0 Hz, C*H*HOR], 4.14 [1 H, dd, *J* = 8.2, 6.0 Hz, CH*H*OR], 4.38 [1 H, (app. t)(app. t), *J* = 7.2, 7.0, 6.0, 5.5 Hz, CH(OR)], 9.22 (1 H, s, CHO). ^{13}C NMR (67 MHz, $CDCl_3$): δ = 25.8 (CH_3), 26.8 (CH_3), 29.5 (CH_3), 45.3 (CH_2), 67.0 (C), 69.9 (CH_2), 72.9 (CH), 81.2 (C), 98.8 (C), 109.3 (C), 176.8 (CH).
(*E*)-Enynone 17
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.37 [3 H, s, C*H*$_3$C(OR)$_2$CH$_3$], 1.42 [3 H, s, C*H*$_3$C(OR)$_2$C*H*$_3$], 1.60 (3 H, s, C*H*$_3$COH), 1.96 [1 H, d(AB)d, *J* = 14.1, 5.5 Hz, CH(OR)C*H*H], 2.13 [1 H, d(AB)d, *J* = 14.1, 7.0 Hz, CH(OR)CH*H*], 2.44 (3 H, s, CH_3CO), 2.96 [1 H,(br) s, OH), 3.65 (1 H, dd, *J* = 8.2, 7.5 Hz, C*H*HOR], 4.14 (1 H, dd, *J* = 8.2, 6.0 Hz, CH*H*OR), 4.27 [2 H, q, *J* = 7.1 Hz, $CO_2CH_2CH_3$], 4.40–4.32 [1 H, m, CH(OR)], 6.80 (1 H, s, C=CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 25.8 (CH_3), 26.8 (CH_3), 29.9 (CH_3), 30.4 (CH_3), 45.4 (CH_2), 61.8 (CH_2), 67.5 (C), 69.9 (CH_2), 73.1 (CH), 79.0 (C), 108.2 (C), 109.1 (C), 122.5 (CH), 143.0 (C), 163.7 (C), 198.5 (C). ESI-MS: *m/z* calcd for $C_{17}H_{24}O_6Na^+$: 347.1465; found: 347.1472 [MNa^+]

(8) **(*E*)-Enynone 20**
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.62 (3 H, s, CH_3COR), 1.73 [1 H, d(AB)d, *J* = 13.1, 2.4 Hz, CH(OR)C*H*^{eq}H], 1.85 [1 H, d(AB)d, *J* = 13.1, 11.8 Hz, CH(OR)CH*H*^{ax}], 2.03 [1 H,(br) s, OH], 2.45 (3 H, s, CH_3CO), 3.63 [1 H, d(AB)d(br), *J* = 11.9, 5.8 Hz, CHC*H*HOH], 3.74 [1 H, d(AB)(app. t)(br), *J* = 11.9, ca. 3 Hz, CHCH*H*OH], 3.80 [3 H,(br) s, CH_3OAr), 4.17–4.24 [1 H, m, CH(OR)], 4.30 (2 H, q, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 5.93 [1 H, s, ArCH(OR)$_2$], 6.84 (1 H, s, C=CH), 6.90 [2 H, d(AA′XX′), *J* = 8.7 Hz, ArH), 7.46 [2 H, d(AA′XX′), *J* = 8.7 Hz, ArH]. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (CH_3), 29.3 (CH_3), 30.4 (CH_3), 38.2 (CH_2), 55.3 (CH_2), 61.9 (CH_3), 65.3 (CH_2), 70.8 (C), 74.6 (CH), 82.5 (C), 97.4 (CH), 106.0

(C), 113.7 (2 CH), 122.3 (CH), 127.8 (2 CH), 130.5 (C), 143.0 (C), 160.2 (C), 165.3 (C), 193.6 (C). ESI-MS: *m/z* calcd for $C_{22}H_{26}O_7Na^+$: 425.1571; found: 425.1566 [MNa^+].

(9) For a recent study with 1-alkynyl-2-carbonyl quinoline substrates, see: Godet, T.; Vaxelaine, C.; Michel, C.; Milet, A.; Belmont, P. *Chem. Eur. J.* **2007**, *13*, 5632; and references cited therein.

(10) **Substituted Furan 25**

Isolated as a ca. 3:2 mixture of *E*/*Z*-isomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ [major isomer (integrating for 60%)] = 1.35 [3 H, s, C*H*$_3$C(OR)$_2$CH$_3$], 1.35 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$], 1.44 [3 H, s, $CH_3C(OR)_2CH_3$], 1.87 (3 H, s, $CH_3C{=}C$), 2.58–2.43 [2 H, m, CH(OR)C*H*$_2$], 2.60 (3 H, s, FurCH$_3$), 3.46 (3 H, s, CH_3O), 3.65 (1 H, app. t, *J* = 8.1, ca. 7 Hz, C*H*HOR), 4.05 (1 H, dd, *J* = 8.1, 6.0 Hz, CH*H*OR), 4.20–4.26 [1 H, m, C*H*(OR)], 4.29 (2 H, q, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 6.60 (1 H, s, FurH); δ [minor isomer (integrating for 40%)] = 1.34 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.35 [3 H, s, $CH_3C(OR)_2CH_3$], 1.41 [3 H, s, $CH_3C(OR)_2CH_3$], 1.87 (3 H, s, $CH_3C{=}C$), 2.58–2.43 [2 H, m, CH(OR)C*H*$_2$], 2.59 (3 H, s, FurCH$_3$), 3.47 (3 H, s, CH_3O), 3.53 (1 H, app. t, *J* = 8.1, ca. 7 Hz, C*H*HOR), 4.01 (1 H, dd, *J* = 8.1, 6.0 Hz, CH*H*OR), 4.20–4.26 [1 H, m, C*H*(OR)], 4.29 (2 H, q, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 6.69 (1 H, s, FurH). ^{13}C NMR (HMQC-HMBC, 400 MHz, $CDCl_3$): δ (major isomer) = 13.9 (CH_3), 14.4 (CH_3), 18.0 (CH_3), 25.7 (CH_3), 26.9 (CH_3), 35.9 (CH_2), 58.5 (CH_3), 60.1 (CH_2), 69.5 (CH_2), 74.9 (CH), 108.7 (C), 111.4 (CH), 114.4 (C), 120.0 (C), 141.8 (C), 146.7 (C), 158.4 (C), 163.9 (C); δ (minor isomer) = 13.9 (CH_3), 14.4 (CH_3), 16.2 (CH_3), 25.7 (CH_3), 26.8 (CH_3), 36.6 (CH_2), 58.3 (CH_3), 60.1 (CH_2), 69.1 (CH_2), 74.9 (CH), 108.9 (C), 111.1 (CH), 114.4 (C), 120.5 (C), 142.3 (C), 146.6 (C), 158.7 (C), 163.9 (C). ESI-MS: *m/z* calcd for $C_{18}H_{26}O_6Na^+$: 361.1622; found: 361.1618 [MNa^+].

(11) **Enol Ether Cyclic Ketal 28**

Isolated as a 1:1 mixture of ketal epimers.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.48 [3 H, s, C*H*$_3$C(OR)], 1.671 and 1.674 [1 H, 2 × ddd, *J* = 13.1, 11.9, 1.3 Hz, CH(OR)C*H*^{ax}H], 1.73 and 1.74 [3 H, 2 × s, C*H*$_3$C(OCH$_3$)], 1.99 [1 H,(br) dd, *J* = 7.7, 5.3 Hz, OH], 2.33 and 2.39 [1 H, 2 × dd, *J* = 13.1, 2.1 Hz, CH(OR)CH*H*^{eq}], 3.13 and 3.16 (3 H, 2 × s, CH_3OCOR), 3.61–3.73 (2 H, m, CH_2OH), 3.80 (3 H, s, CH_3OAr), 3.96–4.03 [1 H, m, C*H*(OR)CH_2OH], 4.29 (2 H, q, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 4.89 and 4.91 [1 H, 2 × d, *J* = 1.3 Hz, CH=C(OR)], 5.72 and 5.73 [1 H, 2 × s, ArCH(OR)$_2$], 6.90 [2 H, d(AA′XX′), *J* = 8.6 Hz, ArH], 7.02 and 7.03 (1 H, 2 × s, $CH{=}CCO_2R$), 7.44 [2 H, d(AA′XX′), *J* = 8.6 Hz, ArH].

^{13}C NMR + HMQC (400 MHz, $CDCl_3$): δ = 14.2 (CH_3, 1.33), 24.4 and 24.6 (CH_3, 1.73 and 1.74), 29.3 (CH_3, 1.48), 36.0 (CH_2, 1.67, 1.73, 1.74), 50.57 and 50.62 (CH_3, 3.13 and 3.16), 55.3 (CH_3, 3.80), 61.0 (CH_2, 4.29), 65.9 (CH_2, 3.61–3.73), 75.08 and 75.13 (CH, 3.96–4.03), 75.34 and 75.36 (C), 96.53 and 96.56 (CH, 5.72 and 5.73), 110.17 and 110.21 (CH, 4.89 and 4.91), 113.7 (2 CH, 6.90), 114.2 (C), 127.6 (2 CH, 7.44), 131.3 (C), 134.3 and 134.4 (C), 137.4 and 137.5 (CH, 7.02 and 7.03), 153.25 and 153.32 (C), 160.0 (C), 161.8 (C). ^{1}H NMR + HMBC (400 MHz, $CDCl_3$): δ = 1.33 (61.0), 1.48 (36.0, 75.4, 110.2), 1.67 (29.3, 65.9, 75.1, 75.3, 110.2), 1.73 and 1.74 (50.6, 114.2, 134.3 and 134.4), 1.99 (–), 2.33 and 2.39 (75.1, 75.3), 3.13 and 3.16 (114.2), 3.61–3.73 (75.1), 3.80 (160.0), 3.96–4.03 (–), 4.29 (14.2, 161.8), 4.89 and 4.91 (29.3, 36.0, 137.4 and 137.5, 153.3), 5.72 and 5.73 (75.1, 127.5), 6.90 (113.7, 131.3, 160.0), 7.02 and 7.03 (114.2, 153.3, 161.8), 7.44 (96.5, 113.7, 127.5, 160.0). ^{1}H NMR + COSY (400 MHz, $CDCl_3$): δ = 1.33 (4.29), 1.48 (–), 1.67 (2.33 and 2.39, 3.96–4.03, 4.89 and 4.91), 1.73 and 1.74 [7.02 and 7.03 (w)], 1.99 (3.61–3.73), 2.33 and 2.39 (1.67, 3.96–4.03), 3.13 and 3.16 (–), 3.61–3.73 (1.99, 3.96–4.03), 3.80 (6.90), 3.96–4.03 (1.67, 2.33 and 2.39, 3.61–3.73), 4.29 (1.33), 4.89 and 4.91 (1.67, 7.02 and 7.03), 5.72 and 5.73 (7.44), 6.90 (3.80, 7.44), 7.02 and 7.03 [4.89 and 4.91, 1.73 and 1.74 (w)], 7.44 (5.72 and 5.73, 7.44). ESI-MS: *m/z* calcd for $C_{23}H_{30}O_8Na^+$: 457.1824; found: 457.1833 [MNa^+].

Substituted Furan 29

Isolated as a ca. 3:2 mixture of *E*/*Z*-isomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ [major isomer (integrating for 58%)] = 1.356 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.88 (3 H, s, $CH_3C{=}C$), 2.05 [1 H,(br)s, CHO*H*), 2.29 (1 H, s, CH_2OH), 2.31 (1 H, dd, *J* = 13.8, 5.2 Hz, =CC*H*H), 2.49 (1 H, dd, *J* = 13.8, 8.6 Hz, =CCH*H*), 2.59 (3 H, s, FurCH$_3$), 3.46 (1 H,(br) dd, *J* = 11.5, 6.5 Hz, C*H*HOH), 3.478 (3 H, s, CH_3O), 3.62–3.68 (1 H, m, CH*H*OH), 3.84–3.93 (1 H, m, C*H*OH), 4.298 (2 H, q, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 6.66 (1 H, s, FurH); δ [minor isomer (integrating for 42%)] = 1.359 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 1.86 (3 H, s, $CH_3C{=}C$), 2.29 (1 H, s, CH_2OH), 2.36 [1 H, d(AB)d, *J* = 13.1, 5.8 Hz, =CC*H*H], 2.51 [1 H, d(AB)d, *J* = 13.1, 8.1 Hz, =CCH*H*], 2.56 [1 H, d(br), *J* = 5.3 Hz, CHO*H*], 2.61 (3 H, s, FurCH$_3$), 3.55 [1 H,(br) d(app. t), *J* = 11.2, 4.6 Hz, C*H*HOH), 3.481 (3 H, s, CH_3O), 3.62–3.68 (1 H, m, CH*H*OH), 3.84–3.93 (1 H, m, C*H*OH), 4.303 (2 H, q, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 6.63 (1 H, s, FurH). ESI-MS: *m/z* calcd for $C_{15}H_{22}O_6Na^+$: 321.1309; found: 321.1297 [MNa^+].

