Supplementary Material

Complementary Amphiphilic Ribonucleotides Confined into Nanostructured Environments

R. Angelico, L. Ambrosone, A. Ceglie, I. Losito, G. De Zio and F. Palmisano

Figure S1. MS/MS spectrum (Collisional Energy: 35%) and product ion assignments for the $[M-H]^-$ ion of the tri-alkylated derivative of UMP (*m/z* 876.5), detected after 118 days in reaction mixtures involving only UMP.

Square brackets indicate that R or R' groups can be linked (through the starred carbon atom) either to the Uracyl N_3 atom or to one of the two OH groups arising from tautomerization of -NH-C=O to -N=C-OH.

The product ion compatible with contemporary alkylation of both ribose OH groups was excluded from regioisomeric ions having m/z 691.3, since no further MS/MS signal confirmed that possibility. See Ref. 5 for further details on fragments already observed in the MS/MS spectrum of bi-alkylated UMP.

Figure S2. MS/MS spectrum (Collisional Energy: 35%) and product ion assignments for the $[M-H]^-$ ion of the tri-alkylated derivative of AMP (*m/z* 899.3), detected after 118 days in reaction mixtures involving only AMP.

Note that:

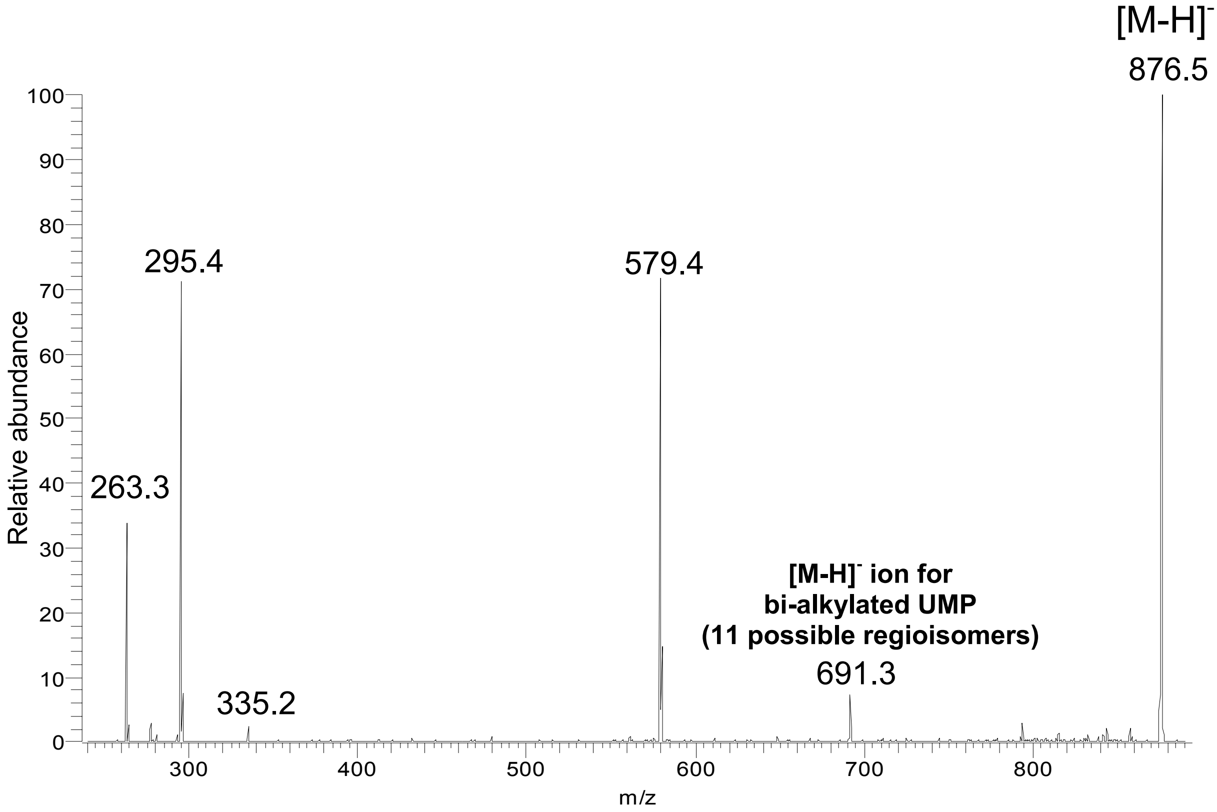
1) the ion with m/z 579.2 has the same structure proposed in Figure S1 (R corresponds to R_1 in this case);

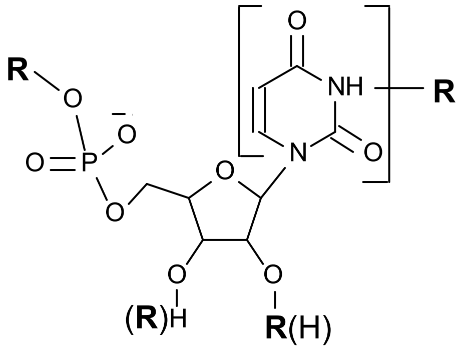
2) double alkylation on the NH_2 group, hypothesized for the fragment ion with m/z 687.3, is the only reasonable possibility for double alkylation on the adenine ring and was observed for the tri-alkylated AMP derivative but never for the bi-alkylated one (see Ref. 5). In this case the linkage between a hydroxy-dodecyl moiety and the adenine N_1 atom (compatible also with fragments at m/z 502.5 and 332.4), is likely formed during fragmentation, as a result of hydroxy-dodecyl migration from an alkylated OH on ribose to the adenine N_1 atom, concomitant with ribose detachment;

3) alternative structures for fragment ions at m/z 634.5, 502.5 and 332.4, having two hydroxyl-dodecyl groups on the adenine NH_2 cannot be excluded, although they are less likely than those reported;

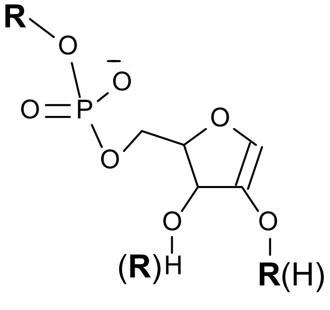
4) only in the case of adenine NH_2 group the nucleophilic attack can occur also to the more hindered carbon atom of the DE epoxidic ring (thus leading to a linkage with a R_2 group). See Ref. 5 for further details on this aspect and on fragmentations already observed in the MS/MS spectrum of bi-alkylated AMP (e.g. the presence of a CH_3 group on an alkylation site, involving the loss of n-undecanal from a previously linked R_1 group).

Figure S1

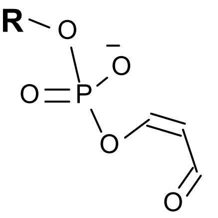




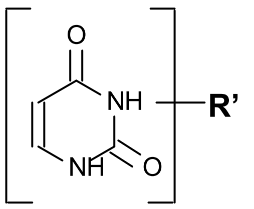
876.5



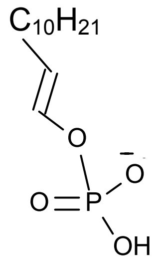
579.4



335.2



295.4



263.3

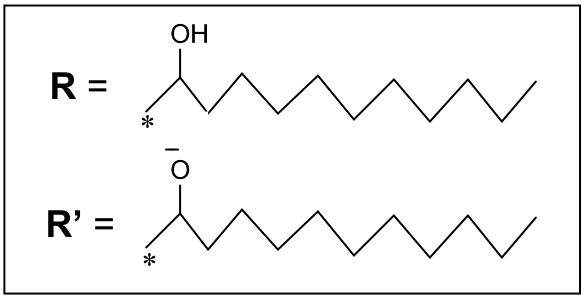
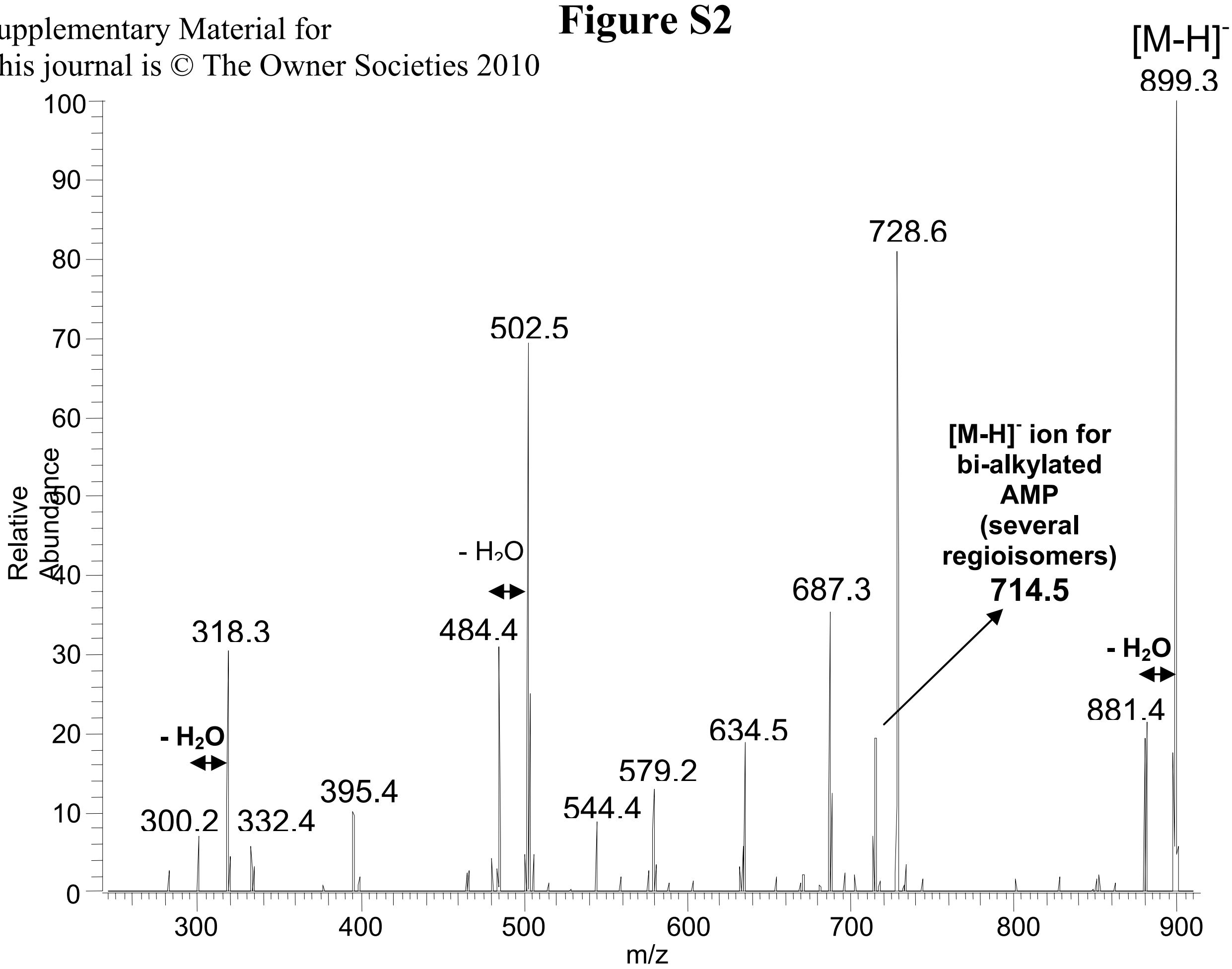
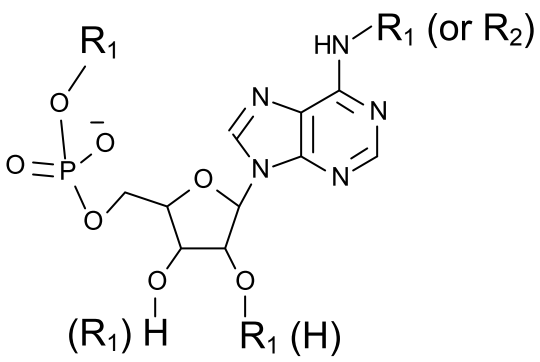


Figure S2

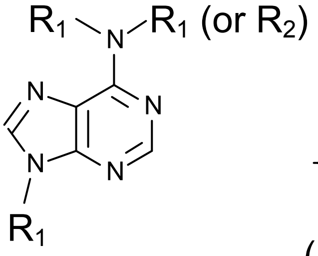




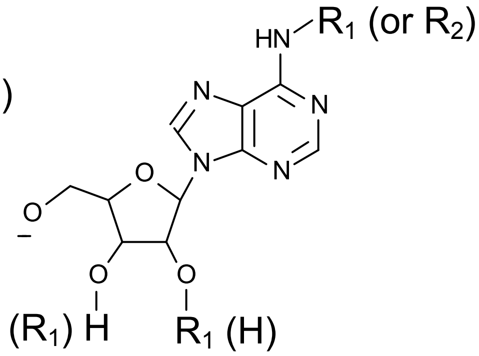
899.3

728.6 (one of the R_1 groups replaced by a CH_3)

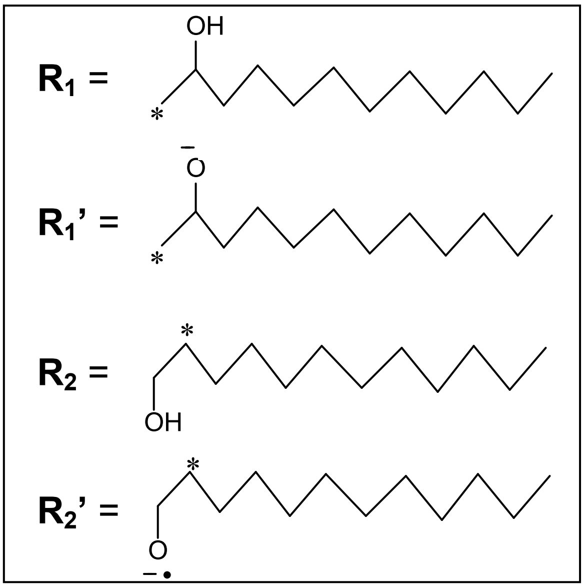
544.4 (one R_1 or R_2 group replaced by H and one R1 group replaced by CH_3)

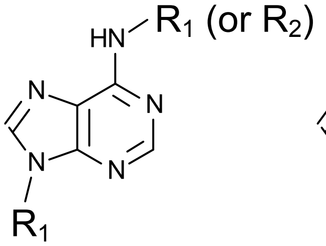


687.3

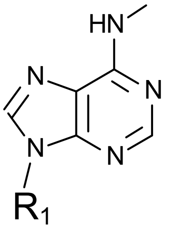


634.5

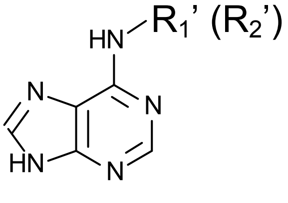




502.5



332.4



318.5