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Assessment of casein phosphopeptide profile in *in vitro* digestates of Trentingrana PDO cheese

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1 1 **Assessment of casein phosphopeptide profile in *in vitro* digestates of Trentingrana PDO cheese**

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21
22 10 **Abstract**

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24 11 Two different *in vitro* static gastrointestinal digestion (GID) protocols were applied to investigate the
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26 12 profile of casein phosphopeptides (CPPs) released from protected designation of origin (PDO)
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28 13 Trentingrana cheese. CPPs in the gastrointestinal digestates were selectively precipitated and identified by
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30 14 ultra-performance liquid chromatography coupled to high-resolution mass spectrometry. Digestion
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32 15 parameters adopted during gastric and intestinal phases of the two GID procedures were pivotal in the
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34 16 resulting CPPs patterns. A standardized digestive protocol mimicking *in vivo* conditions, made available
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36 17 half of the CPPs identified following a simpler procedure based only on the action of pepsin and
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38 18 pancreatin. Independently of the GID protocol used, the mono-phosphorylated CPPs were the most
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40 19 abundant (>55%) followed by bi- (23–29%) and tri-phosphorylated (8–18%) peptides. Alfa_{s1}-casein was
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42 20 the parent fraction mainly contributing to CPPs release. The number of peptides containing the
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44 21 biofunctional cluster sequence SerP-SerP-SerP-Glu-Glu almost overlapped in the digestates from the two
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46 22 GID models. About a half of these peptides was common between the two GID models, and a large part
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48 23 of them derived from α_{s2}- and β-caseins. Overall, results of this investigation proved that CPPs profiles of
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50 24 *in vitro* digestates of Trentingrana were similar to those previously reported for Grana Padano PDO using
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52 25 the same digestion protocols.

Keywords: casein phosphopeptides, *in vitro* gastrointestinal digestion, ultra-performance liquid chromatography, high-resolution mass spectrometry.

Introduction

Trentingrana cheese is a long-ripened hard cooked Italian cheese obtained from raw partially-skimmed milk. It is produced in the restricted Alpine region of Trentino, and it plays an economically relevant role for this geographical zone of Italy. The cheesemaking protocol stands out from that of Grana Padano PDO (one of the most widespread long-ripened hard cooked Italian variety) mainly for the limiting rules in relation to the feeding regime of cows (silage not permitted) as well as for the forbidden use of lysozyme in vat milk. As it occurs for Grana Padano cheese, important proteolysis characterizes the ripening of Trentingrana. This phenomenon is due to the action of proteinases and peptidases of natural whey starter mainly consisting of *Lactobacillus helveticus*. The action of these enzymes on casein (CN) [1] has been studied, and the formation of CN phosphopeptides (CPPs) has been proved in Grana Padano [2, 3]. Likewise, their release during cheese ripening by action of proteolytic enzymes such as milk-native, milk-clotting and/or microbial proteinases is acknowledged for other hard long-ripened cheeses such as Comté and Parmigiano Reggiano [2, 4–7]. Casein phosphopeptides are naturally produced in dairy products following milk fermentation by starter cultures adopted during cheese milk processing [8].

Casein phosphopeptides have been reported to possess several biological functions [9], including sequestering activity of metal ions [10], bone calcification [11], anticariogenicity [12], opioid-like, immunomodulatory and citomodulatory activities [13, 14]. An enhancing effect of CPPs on calcium absorption has been demonstrated by *in vitro* assays [15]. In particular, recent investigations proved the ability of Grana Padano and Trentingrana digestates to exert intestinal cell calcium uptake [16].

In addition to dairy-fermented products, food-borne CPPs may form *in vivo* during several steps of digestion of CN and the milk products thereof. The presence of CPPs was revealed in human intestinal fluids after milk or yogurt ingestion [17], demonstrating their resistance to gastrointestinal passage.

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3 53 Recently, CPPs were detected in human plasma after ingestion of Parmigiano Reggiano cheese [18].
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5 54 Generally, *in vitro* digestibility tests are exploited as a simple and fast tool to mimic *in vivo* conditions.
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7 55 However, the variability of the adopted digestion parameters is potentially reflected by the diversity of the
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10 56 obtained results. In this regard, the CPPs profiles of Grana Padano digestates were recently studied using
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12 57 two different static *in vitro* gastrointestinal digestion (GID) protocols [3]. In detail, a two-step model
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14 58 adopting single enzymes (porcine pepsin and pancreatin) was compared with an internationally accepted
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16 59 model for *in vitro* GID studies including the oral, gastric and small intestinal digestions.

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18 60 To the best of our knowledge, neither the CPPs profile of Trentingrana digestates was reported so
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20 61 far nor the effect of the adopted GID protocol was assessed. Therefore, the primary goal of the current
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22 62 work consisted in the evaluation of the CPPs profiles of Trentingrana cheese digestates obtained by the
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24 63 two above-mentioned GID protocols by ultra-performance liquid chromatography coupled to high-
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26 64 resolution mass spectrometry (UPLC-HR-MS). Additional focus was addressed to the effect on number
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28 65 and type of triphosphorylated CPPs, which were characterized by the polar acidic cluster sequence SerP-
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30 66 SerP-SerP-Glu-Glu (sssEE), which is known to be the binding site of several divalent cations [24, 28].
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32 67 The peptidic patterns of Trentingrana cheese digestates in comparison to the homologous ones of Grana
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34 68 Padano reported in a previous research study [3] were also discussed.

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40 70 **Materials and methods**

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44 72 Distilled water was purified with a MilliQ ULTRA system (EMD Millipore, Billerica, MA, USA). All
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46 73 chemicals were from Sigma-Aldrich (St. Louis, MO, USA).

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50 75 *Cheese samples*

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55 77 Three samples of Trentingrana were manufactured by a dairy factory belonging to the “Grana Padano
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57 78 Consortium” according the standard cheese manufacturing procedure, and aged 13, 19 and 26 months.

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80 *Simulated gastrointestinal digestion*

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82 Cheese samples were submitted to two *in vitro* static GID protocols, as previously described [3]. A cheese

83 wedge (approximately 2.5 kg) representative of the whole wheel was cut and grated after rind removal. In

84 the first method, hereinafter referred to as PePan, an aliquot of grated cheese (4.5 g) was suspended in

85 MilliQ-treated water and digested with 0.02 g (10000 U) of porcine pepsin per g of cheese. The

86 suspension was adjusted to pH 2.0 (with 1 M HCl) and incubated at 37 °C for 2 h. Subsequently, porcine

87 pancreatin (4 x USP specifications) and bile salts (0.03 g g⁻¹ of cheese) were added to gastric digestate.

88 The suspension adjusted to pH 7.0 (with 1 M NaHCO₃) was incubated at 37 °C for 2 h. In the second *in*

89 *vitro* GID protocol (hereinafter COST) the cheese samples were sequentially digested in three simulated

90 fluids (salivary, SSF; gastric, SGF and duodenal, SDF) prepared as previously reported [19, 20]. In detail,

91 5 mL of SSF (pH 7.0) were added to the cheese sample (5 g), and it was ground for 2 min to mimic the

92 mastication. The mixture, supplemented with SGF (10 mL) and porcine pepsin (1000 U mL⁻¹ SGF), was

93 submitted to digestion at 37 °C for 2 h after adjusting the pH to 3.0 by addition of 1 M HCl. After gastric

94 phase, the digestate was supplemented with 20 mL of SDF and bile salts (10 mM). The enzymes involved

95 in the intestinal digestion consisted of porcine trypsin (100 U mL⁻¹ SDF), bovine chymotrypsin (50 U mL⁻¹

96 SDF), porcine intestinal lipase (2000 U mL⁻¹ SDF) and co-lipase (molar ratio of lipase to co-lipase 1:2).

97 The hydrolysis was carried out at pH 7.0 at 37 °C for 2 h. The reaction was stopped by adding a protease

98 inhibitor (AESFB, Roche, Mannheim, Germany) up to a final concentration of 1 mM. Digestion blanks

99 for each protocol were also prepared. All digested samples were immediately frozen (-40 °C) and freeze-

100 dried. The digestions were performed in triplicate the same day.

102 *Isolation of CPPs*

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3 104 Casein phosphopeptides in gastrointestinal digestates were selectively precipitated in presence of CaCl₂
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5 105 and ethanol according to Reynolds et al. [21]. Briefly, 0.4 g of freeze dried digestates, re-suspended in 10
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7 106 mL of MilliQ-treated water, were supplemented with 10% (w/v) CaCl₂ and an equal volume of 99.8% v/v
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10 107 ethanol. After adjusting pH to 4.6 or 8.0, the suspension was centrifuged at 12000 g for 10 min at 10 °C.
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12 108 The precipitate was washed with 50 % (v/v) ethanol. Subsequently, ethanol was removed under N₂ flow,
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14 109 and precipitated peptides were resuspended in 2 mL of MilliQ-treated water with 0.1 % (v/v) formic acid,
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16 110 filtered through a PVDF membrane (0.22 µm, EMD Millipore) and stored at –40 °C before analysis.
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21 112 *Identification of CPPs by Ultra-performance liquid chromatography-high resolution mass spectrometry*
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23 113 *(UPLC-HR-MS)*
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27 115 Casein phosphopeptides were identified by UPLC-HR-MS. An Acquity UPLC module (Waters, Milford,
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29 116 MA, USA) was coupled to a Q Exactive hybrid quadrupole-Orbitrap mass spectrometer (Thermo
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31 117 Scientific, San Jose, CA, USA). Analytical conditions and settings previously described by Cattaneo et al.
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33 118 [3] were adopted. Identification of CPPs was carried out using Proteome Discover 1.4 software (Thermo
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35 119 Scientific). Peptides were identified using the database of *Bos taurus* (UniProt taxon ID 9913) CNs.
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40 121 **Results and discussion**
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44 123 This study aimed at applying two *in vitro* static protocols (PePan and COST) for GID of Trentingrana
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46 124 cheese and evaluating the CPPs profiles in the derived digestates. The digestion approach based on a two-
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48 125 step model (PePan) adopting porcine pepsin and pancreatin was compared with the standardized COST
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50 126 procedure approved by the international scientific community [22]. The latter one included also an oral
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52 127 phase and adopted digestive fluids with specified physiological parameters (for gastric and intestinal
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54 128 steps). The COST protocol mimics the *in vivo* conditions of cheese digestion [22]. In both cases, CPPs
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56 129 were purified from the gastrointesitinal hydrolysates by precipitation using Ca²⁺ and ethanol under two
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different pH conditions (4.6 and 8.0) to ensure full recovery of different phosphorylated peptides [3]. The CPPs-enriched precipitates were solubilized (as described in "Materials and Methods") and subsequently analyzed by UPLC-HR-MS. All the identified CPPs are listed by retention time, pH value, of purification, digestion method and cheese sample in the supplementary data (Tables S1 and S2). The total ion current chromatograms of the purified Trentingrana digesta produced upon PePan and COST digestion are shown in Figs. 1 and 2, respectively. Chromatographic profiles appeared clustered as a function of either the GID model or the pH adopted for the CPPs isolation, but did not depend on the ripening time of the analyzed cheese samples. In detail, as observed in a previous research study on Grana Padano cheese [3], the pH value used to purify CPPs from the digestates affected the recovery of CPPs. Indeed, the CPPs profiles of precipitates at pH 8.0 were less complex than those obtained at pH 4.6. The precipitation at pH 4.6 exhibited lower specificity, allowing co-precipitation of other peptides (results not shown).

Casein phosphopeptides released adopting the PePan protocol were 300, 280 and 279 in 13, 19 and 26 months aged Trentingrana cheese, respectively (Table 1). These numbers, independently of the adopted pH conditions for CPPs isolation, were similar to those recorded for Grana Padano cheese upon the same GID protocol [3]. Following COST procedure, the number of released CPPs reduced to 56–57%. Also in this case data reflected those previously reported for the Grana Padano cheese digesta. Parameters adopted during GID were pivotal in promoting this difference. In particular, the higher pH value exploited for the gastric digestion in COST model (pH 3.0 instead of pH 2.0 of PePan procedure) likely partially hindered pepsin activity [23]. In addition, in the PePan protocol, the intestinal step was carried out with porcine pancreatin, an enzymatic cocktail generally used to generate CPPs [24]. Together with trypsin, pancreatin juices contain also chymotrypsin (used also in COST protocol), carboxypeptidase and other peptidases, thus exhibiting a broader proteolytic activity [25]. Peptides generated via both digestion protocols were almost of the same length and varied from 6 to 24 amino acid residues. Following the digestion by COST protocol, the contribution of parent proteins, from which CPPs were released, was α_{s1} -CN > α_{s2} -CN > β -CN, with a relative abundance of a number of the released peptides of 42–48%, 31–35% and 21–23%, respectively, in the three differently aged cheese samples. Following the

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3 156 PePan digestion, this ranking changed to α_{s1} -CN > β -CN > α_{s2} -CN with corresponding percentages of 43–
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5 157 52%, 26–29% and 21–26%. We observed that some bi-phosphorylated CPPs deriving from parent α_{s1} -
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8 158 CN, identified in our investigation applying both GID protocols, namely f(43–50)2P, f(43–52)2P and
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10 159 f(43–58)2P, exactly matched those recorded by Caira et al. [18] in plasma samples from individual
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12 160 subjects after a Parmigiano Reggiano enriched diet. Only a small number of CPPs (from 1 to 6) deriving
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14 161 from κ -CN was revealed (Table 1), being the PePan protocol the major contributor.

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16 162 In addition to the total number of CPPs released upon GID of Trentingrana cheese samples, we
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18 163 investigated the phosphorylation degree of those CPPs. At all stages of ripening and independently of the
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20 164 GID protocol used, mono-phosphorylated peptides prevailed (>55% of total CPPs). This evidence was
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22 165 recorded also by Adt et al. [26] in *in vitro* gastrointestinal digestates of Beaufort cheese. Bi- and tri-
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24 166 phosphorylated peptides occurred to a lower extent (i.e., 23–29% and 8–18% of total CPPs, respectively).
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26 167 However, some variability regarding this trend was observed when each parent CN fraction was taken
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28 168 into consideration. The number of mono- and bi-phosphorylated peptides from α_{s1} -CN was almost the
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30 169 same. Meanwhile, CPPs from β -CN gave rise mainly to mono-phosphorylated sequences. This last
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32 170 evidence matched with the results previously reported for Grana Padano cheese digestates [3].

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35 171 The adopted GID protocols originated 86–94 common CPPs. In particular, the sharing affected
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37 172 about a half and one third of CPPs released by COST and PePan protocols, respectively. Regarding the
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39 173 CN fractions, the CPPs shared between the two digestates were 40–49, 25–29 and 16–22 for α_{s1} -CN, β -
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41 174 CN and α_{s2} -CN, respectively. Taking into account mono-, bi- and tri-phosphorylated peptides, total
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43 175 common peptides in the analyzed Trentingrana samples were 57–62, 18–27 and 6–12, respectively.

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46 176 It is known that κ -CN sequence has only one phosphorylated Ser (residue 149) [27]. However,
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48 177 Thr residues with different degrees of phosphorylation were identified at C-terminus. We revealed both
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50 178 peptides with phosphorylated Ser₁₄₉ and the peptides with 1 to 3 phosphorylated Thr residues. In all
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52 179 digestates, these latter CPPs formed from glycomacropeptide, which is an open flexible region of κ -CN
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54 180 and for this reason is more accessible to enzymatic hydrolysis. Only PePan digestates contained the κ -CN
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56 181 fragment f(125–136)3P with tri-phosphoryl residues of Thr.

Some phosphorylated peptides [α_{s1} -CN f(109–119), α_{s1} -CN f(110–120), β -CN f(33–48)] found upon application of both digestion protocols matched those identified *in vivo* in the gastrointestinal tract of humans by Boutrou et al. [29]. Other peptides corresponded to those found in the digestive tract of mini-pigs and rats: α_{s1} -CN f(40–52), α_{s1} -CN f(40–58), α_{s1} -CN f(40–61), α_{s1} -CN f(43–58), α_{s1} -CN f(61–74), α_{s1} -CN f(66–74), α_{s1} -CN f(110–119), α_{s2} -CN f(124–137), α_{s2} -CN f(138–149), α_{s2} -CN f(138–150), β -CN f(7–24), β -CN f(29–45), β -CN f(30–52), β -CN f(33–52) [30, 31].

The evaluation of the occurrence of the polar acidic cluster sssEE in digestates of Trentingrana was another target of our investigation. More than 40% of tri-phosphorylated CPPs contained this motif. Such sequence, common to α_{s1} -CN (residues 66–70), α_{s2} -CN (residues 8–12 and 56–60) and β -CN (residues 17–21), was identified in 30 peptides considering both GID protocols. Some research studies report that the characteristic sequence sssEE is particularly resistant to further hydrolysis and it constitutes the binding site of several divalent cations [24, 28]. The resistance of this motif was observed in long ripened cheeses and attributed to the high concentration of negative charges of phosphate residues present as monoesters of Ser [32]. In our research, CPPs containing the phosphorylated cluster sssEE were 10–18 and 15–20 after GID with PePan and COST protocols, respectively. Overall, twelve of these peptides were common among all analyzed Trentingrana cheese samples (Fig. 3). When expressed on overall tri-phosphorylated CPPs, this cluster sequence was more abundant following COST (53–74%) rather than PePan protocol (36–42%). Adopting this last protocol, peptides with motif sssEE derived from β -CN >> α_{s2} -CN > α_{s1} -CN. Differently, upon COST approach parent fractions were β -CN = α_{s2} -CN >> α_{s1} -CN. Common fragments resistant to *in vitro* GID were α_{s1} -CN f(65–74), α_{s2} -CN f(7–13), β -CN f(16–22), β -CN f(16–24) and β -CN f(17–24). Alfa_{s1}-CN formed only fragments f(64–74) and f(65–74), likely deriving from the common parent plasmin-mediated α_{s1} -CNf(1–79)7P [2]. Two CPPs which included sssEE amino acid sequence derived from peptide α_{s1} -CN f(64–74) that was characterized by Asn₇₄ as C-terminal end. Among these, the fragment f(66–74) was also identified *in vivo* in the intestinal content of minipigs fed a CN-based diet [33]. Summing up, thirteen CPPs including the sequence sssEE derived from α_{s2} -CN (three of which were common to both protocols). PePan digestates distinguished for the

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3 208 occurrence of α_{s2} -CN f(1–12) in samples at all stages of ripening. Four other peptides belonged to parent
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5 209 fragments α_{s2} -CN f(7–13) and α_{s2} -CN f(53–70). Fragments with Ser₅₃ residue at the N-terminal end likely
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7 210 resulted by chymotrypsin action, and were identified after both digestive processes. CPPs from α_{s2} -CN
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9 211 released by COST protocol were more abundant (n = 11) and almost all of them derived from α_{s2} -CN f(5–
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11 212 15) and f(53–65). Beta-CN yielded the major amount (n = 14) of CPPs with the motif sssEE. In detail, all
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13 213 fragments derived from the parent β -CN f(1–28), as a result of the cleavage at site Lys₂₈-Lys₂₉ by plasmin
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15 214 hydrolysis [34]. This enzyme is active in cheese varieties that are cooked at high temperature, such as
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17 215 Grana-type cheeses, where plasmin is the principal proteolytic agent. In Parmigiano Reggiano, another
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19 216 economically-important long-ripened hard cooked Italian variety, Sforza et al. [7] identified several CPPs
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21 217 from this parent fragment subsequently derived upon the action of exopeptidases of starter lactic acid
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23 218 bacteria after cell death. All fragments revealed in our study belonged to β -CN f(1–25) representing the
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25 219 main CPP revealed in the intestinal content of rats fed a β -CN based diet [35]. Both COST and PePan
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27 220 digestive protocols gave substantially similar CPPs profiles. With the exception of β -CN f(6–24), detected
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29 221 only in 26-mo aged Trentingrana digestate by PePan procedure, all peptides from β -CN containing motif
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31 222 sssEE differed by one to two N-terminal residues and by one to four C-terminal residues (Fig. 3). Most of
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33 223 fragments were characterized by Arg, Ser and Thr at C-terminus, matching with broad cleaving
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35 224 specificity of pancreatin [36]. Overall, both GID procedures released CPPs from all domains of CN
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37 225 fractions containing the sequence sssEE. Digestate profiles obtained in this study were highly
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39 226 homologous to the previous ones obtained for Grana Padano cheese [3].
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51 228 **Conclusions**
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51 230 Sensitive differences in the number of CPPs identified after *in vitro* GID of Trentingrana cheese as a
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53 231 function of the adopted protocol were observed. The harmonized COST procedure made available half of
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55 232 the CPPs identified following PePan simulated digestion, based on the subsequent action of pepsin and
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57 233 porcine pancreatin. On average, the relative degree of phosphorylation of released peptides was similar
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between the two procedures, and it was characterized by the predominance of mono-phosphoryl peptides. It is worth to note that the sssEE-motif containing CPPs were largely predominant among tri-phosphorylated peptides, resulting slightly more abundant after digestion with COST protocol. CPPs with the above-mentioned sequence originated from β -CN shared common domains and differed for one or more residues at both N- or C-terminal end. The fingerprint of CPPs of Trentingrana almost overlapped that of the Grana Padano described in a previous research study [3], independently of the adopted GID model. These evidences confirm both the major role exerted by GID parameters in the release of CPPs in the two above-mentioned cheese varieties and the minor effect of specific cheesemaking steps (i.e., the addition of lysozyme to milk in vat). Summing up, this research provides data useful for the comparison of CPP profile with those of other cheese varieties.

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3 362 **Figure captions**
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7 364 **Figure 1**
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10 365 HR-MS total ion current profiles of Trentingrana cheese digestates (PePan protocol) after CPP enrichment
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12 366 by selective precipitation at pH 4.6 (A) or pH 8.0 (B). Months of ripening are indicated for each cheese
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14 367 sample.
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16 368
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18 369 **Figure 2**
19
20 370 HR-MS total ion current profiles of Trentingrana cheese digestates (COST protocol) after CPP
21
22 371 enrichment by selective precipitation at pH 4.6 (A) or pH 8.0 (B). Months of ripening are indicated for
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24 372 each cheese sample.
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27 373
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29 374 **Figure 3**
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31 375 Casein phosphopeptides containing the motif SerP-SerP-SerP-Glu-Glu (**sssEE**) identified in Trentingrana
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33 376 cheese after *in vitro* gastrointestinal digestion according PePan (▨▨▨), COST (■) or both protocols (⊠).
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35 377 Age of cheese ripening (months) is reported.
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Figure 1

Figure 2

Figure 3

Table 1
Number and phosphorylation degree of CPPs identified in Trentingrana digestates after in vitro GID according **PePan (P)**, **COST (C)** or both (PC) protocols. Age expressed in months; P_d, phosphorylation degree; 1P, mono-phosphorylated CPPs; 2P, bi-phosphorylated CPPs; 3P, tri-phosphorylated CPPs; sssEE, CPPs with SerP-SerP-SerP-Glu-Glu cluster motif.

Age	P _d	αS ₁ -CN			αS ₂ -CN			β-CN			κ-CN			Total CPPs		
		P	C	PC	P	C	PC	P	C	PC	P	C	PC	P	C	PC
13	1P	38	18	24	39	18	14	51	3	23	5	0	1	133	39	62
	2P	42	10	14	19	10	1	2	2	3	0	0	0	63	22	18
	3P	10	7	2	4	12	1	4	5	3	0	0	0	18	24	6
	Total	90	35	40	62	40	16	57	10	29	5	0	1	214	85	86
	sssEE	0	1	1	1	6	1	4	5	3	0	0	0	5	11	5
19	1P	30	13	22	25	15	16	43	4	19	2	0	1	100	32	58
	2P	43	7	16	13	11	2	2	3	1	0	1	0	58	22	19
	3P	21	6	2	4	7	4	7	2	6	1	0	0	33	15	12
	Total	94	26	40	42	33	22	52	9	26	3	1	1	191	69	89
	sssEE	1	3	0	2	6	3	4	2	6	0	0	0	7	11	9
26	1P	34	11	24	24	12	15	40	5	17	1	0	0	98	28	57
	2P	40	7	21	10	10	3	1	1	3	0	0	0	51	18	27
	3P	22	7	4	6	7	1	7	1	5	0	0	1	36	15	10
	Total	96	25	49	40	29	19	48	7	25	1	0	1	185	61	94
	sssEE	0	1	2	3	5	1	7	1	5	0	0	0	10	7	8

Supplementary Table S1. TN_13. Caseinophosphopeptides identified in enriched CPPs isolated from cheese digesta by selective precipitation with pH 8.0 are indicated in black; pH 4.6 are indicated in red; both, pH 8.0 and pH 4.6, are indicated in blue.

Protein fragment			Sequence
α S1-CN	f (	35 - 42	) EKVNELSK
α S1-CN	f (	35 - 50	) EKVNELSKDIGsEsTE
α S1-CN	f (	35 - 52	) EKVNELSKDIGsESTEDQ
α S1-CN	f (	35 - 52	) EKVNELSKDIGsEsTEDQ
α S1-CN	f (	35 - 56	) EKVNELSKDIGsEsTEDQAMED
α S1-CN	f (	36 - 52	) KVNELSKDIGsEsTEDQ
α S1-CN	f (	36 - 56	) KVNELSKDIGsEsTEDQAMED
α S1-CN	f (	37 - 42	) VNELSK
α S1-CN	f (	37 - 45	) VnELSKDIG
α S1-CN	f (	37 - 47	) VNELSKDIGsE
α S1-CN	f (	37 - 52	) VNELSKDIGsESTEDQ
α S1-CN	f (	37 - 52	) VNELSKDIGSEstEDQ
α S1-CN	f (	37 - 52	) VNELSKDIGsEsTEDQ
α S1-CN	f (	37 - 53	) VNELSKDIGsEsTEDQA
α S1-CN	f (	37 - 54	) VNELSKDIGsEsTEDQAM
α S1-CN	f (	37 - 56	) VNELSKDIGsEsTEDQAMED
α S1-CN	f (	39 - 52	) ELSKDIGSEstEDQ
α S1-CN	f (	39 - 52	) ELSKDIGsEsTEDQ
α S1-CN	f (	39 - 56	) ELSKDIGsEsTEDQAMED
α S1-CN	f (	40 - 50	) LSKDIGsEsTE
α S1-CN	f (	40 - 51	) LSKDIGsEsTED
α S1-CN	f (	40 - 52	) LSKDIGSEstEDQ
α S1-CN	f (	40 - 52	) LSKDIGsESTEDQ
α S1-CN	f (	40 - 52	) LSKDIGsEsTEDQ
α S1-CN	f (	40 - 53	) LSKDIGsEsTEDQA
α S1-CN	f (	40 - 52	) LsKDIGsEsTEDQ
α S1-CN	f (	40 - 54	) LSKDIGsEsTEDQAM
α S1-CN	f (	40 - 55	) LSKDIGsEsTEDQAME
α S1-CN	f (	40 - 55	) LSKDIGsEsTEDQAmE
α S1-CN	f (	40 - 56	) LSKDIGsEsTEDQAMED
α S1-CN	f (	40 - 58	) LSKDIGSEstEDQAMEDIK
α S1-CN	f (	40 - 59	) LSKDIGsEsTEDQAMEDIKQ
α S1-CN	f (	40 - 60	) LSKDIGsEsTEDQAMEDIKQM
α S1-CN	f (	41 - 50	) SKDIGsEsTE
α S1-CN	f (	41 - 52	) SKDIGsESTEDQ
α S1-CN	f (	41 - 52	) SKDIGsEsTEDQ
α S1-CN	f (	41 - 53	) SKDIGsEsTEDQA

1				
2	α S1-CN	f (	41 - 54	) SKDIGsEsTEDQAM
3	α S1-CN	f (	41 - 55	) SKDIGsEsTEDQAME
4	α S1-CN	f (	41 - 55	) SKDIGsEsTEDQAmE
5	α S1-CN	f (	41 - 56	) SKDIGsEsTEDQAMED
6	α S1-CN	f (	41 - 56	) SKDIGsEsTEDQAmED
7	α S1-CN	f (	41 - 57	) SKDIGSEstEDQAMEDI
8	α S1-CN	f (	41 - 58	) SKDIGsEsTEDQAMEDIK
9	α S1-CN	f (	41 - 59	) SKDIGsEsTEDQAMEDIKQ
10	α S1-CN	f (	41 - 60	) SKDIGsEsTEDQAMEDIKQM
11	α S1-CN	f (	41 - 61	) SKDIGsEsTEDQAMEDIKQME
12	α S1-CN	f (	41 - 63	) SKDIGsEsTEDQAMEDIKQMEAE
13	α S1-CN	f (	42 - 52	) KDIGsEsTEDQ
14	α S1-CN	f (	42 - 53	) KDIGsEsTEDQA
15	α S1-CN	f (	42 - 56	) KDIGsEsTEDQAMED
16	α S1-CN	f (	42 - 58	) KDIGsEsTEDQAMEDIK
17	α S1-CN	f (	43 - 50	) DIGsEsTE
18	α S1-CN	f (	43 - 52	) DIGsESTEDQ
19	α S1-CN	f (	43 - 52	) DIGsEsTEDQ
20	α S1-CN	f (	43 - 53	) DIGsEsTEDQA
21	α S1-CN	f (	43 - 55	) DIGsEsTEDQAmE
22	α S1-CN	f (	43 - 56	) DIGSEstEDQAMED
23	α S1-CN	f (	43 - 56	) DIGsEsTEDQAMED
24	α S1-CN	f (	43 - 58	) DIGsESTEDQAMEDIK
25	α S1-CN	f (	43 - 58	) DIGsEsTEDQAMEDIK
26	α S1-CN	f (	43 - 58	) DIGsEsTEDQAmEDIK
27	α S1-CN	f (	43 - 59	) DIGsESTEDQAMEDIKQ
28	α S1-CN	f (	43 - 59	) DIGsEsTEDQAMEDIKQ
29	α S1-CN	f (	43 - 59	) DIGsEsTEDQAmEDIKQ
30	α S1-CN	f (	43 - 60	) DIGsEsTEDQAMEDIKQM
31	α S1-CN	f (	43 - 60	) DIGsEsTEDQAmEDIKQM
32	α S1-CN	f (	43 - 61	) DIGsEsTEDQAMEDIKQME
33	α S1-CN	f (	43 - 61	) DIGsEsTEDQAmEDIKQME
34	α S1-CN	f (	43 - 63	) DIGsEsTEDQAMEDIKQMEAE
35	α S1-CN	f (	44 - 52	) IGsEsTEDQ
36	α S1-CN	f (	44 - 58	) IGsEsTEDQAMEDIK
37	α S1-CN	f (	45 - 52	) GsEsTEDQ
38	α S1-CN	f (	46 - 52	) sEsTEDQ
39	α S1-CN	f (	46 - 54	) SEStEDQAM
40	α S1-CN	f (	57 - 65	) IKQMEAEsI
41	α S1-CN	f (	59 - 65	) QMEAEsI
42	α S1-CN	f (	60 - 65	) MEAEsI
43	α S1-CN	f (	65 - 74	) IsssEEIVPN
44	α S1-CN	f (	67 - 74	) sSEEIVPN
45	α S1-CN	f (	67 - 74	) ssEEIVPN
46	α S1-CN	f (	67 - 79	) SsEEIVPNsVEQK
47	α S1-CN	f (	67 - 79	) ssEEIVPNsVEQK
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2	α S1-CN	f (	68 - 74	) sEEIVPN
3	α S1-CN	f (	69 - 78	) EIVPNsVEQK
4	α S1-CN	f (	69 - 79	) EEIVPNsVEQK
5	α S1-CN	f (	73 - 79	) PNsVEQK
6	α S1-CN	f (	80 - 90	) HIqKEDVPsER
7	α S1-CN	f (	80 - 90	) HIQKEDVPsER
8	α S1-CN	f (	104 - 116	) YKVPQLEIVPNsA
9	α S1-CN	f (	104 - 118	) YKVPQLEIVPNsAEE
10	α S1-CN	f (	104 - 119	) YKVPQLEIVPNsAEER
11	α S1-CN	f (	105 - 116	) KVPQLEIVPNsA
12	α S1-CN	f (	105 - 118	) KVPQLEIVPNsAEE
13	α S1-CN	f (	105 - 119	) KVPQLEIVPNsAEER
14	α S1-CN	f (	106 - 119	) VPQLEIVPNsAEER
15	α S1-CN	f (	108 - 119	) QLEIVPNsAEER
16	α S1-CN	f (	108 - 119	) qLEIVPNsAEER
17	α S1-CN	f (	109 - 116	) LEIVPNsA
18	α S1-CN	f (	109 - 118	) LEIVPNsAEE
19	α S1-CN	f (	109 - 119	) LEIVPNsAEER
20	α S1-CN	f (	109 - 119	) LEIVPnsAEER
21	α S1-CN	f (	109 - 120	) LEIVPNsAEERL
22	α S1-CN	f (	109 - 120	) LEIVPnsAEERL
23	α S1-CN	f (	109 - 121	) LEIVPNsAEERLH
24	α S1-CN	f (	110 - 116	) EIVPNsA
25	α S1-CN	f (	110 - 116	) EIVPnsA
26	α S1-CN	f (	110 - 117	) EIVPNsAE
27	α S1-CN	f (	110 - 118	) EIVPNsAEE
28	α S1-CN	f (	110 - 118	) EIVPnsAEE
29	α S1-CN	f (	110 - 119	) EIVPNsAEER
30	α S1-CN	f (	110 - 119	) EIVPnsAEER
31	α S1-CN	f (	110 - 120	) EIVPNsAEERL
32	α S1-CN	f (	110 - 120	) EIVPnsAEERL
33	α S1-CN	f (	110 - 121	) EIVPNsAEERLH
34	α S1-CN	f (	110 - 121	) EIVPnsAEERLH
35	α S1-CN	f (	110 - 121	) EIVPnsAEERLHSM
36	α S1-CN	f (	111 - 119	) IVPNsAEER
37	α S1-CN	f (	111 - 119	) IVPnsAEER
38	α S1-CN	f (	112 - 119	) VPnsAEER
39	α S1-CN	f (	112 - 119	) VPnsAEER
40	α S1-CN	f (	113 - 118	) PNsAEE
41	α S1-CN	f (	113 - 119	) PNsAEER
42	α S1-CN	f (	113 - 119	) PnsAEER
43	α S1-CN	f (	113 - 120	) PNsAEERL
44	α S1-CN	f (	113 - 121	) PNsAEERLH
45	α S1-CN	f (	121 - 131	) HsMKEGIHAQQ
46	α S1-CN	f (	173 - 179	) YTDAPsF
47	α S1-CN	f (	174 - 179	) TDAPsF
48	α S1-CN B	f (	180 - 193	) SDIPNPIGsENSEK
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2	α S1-CN B	f (	180 - 198	) SDIPNPIGSENSEKtTMPL
3	α S2-CN	f (	1 - 12	) KNTMEHVsssEE
4	α S2-CN	f (	1 - 19	) KNTMEHVSsEEsIIsQET
5	α S2-CN	f (	7 - 13	) VsssEES
6	α S2-CN	f (	8&56 - 13&61	) ssSEES
7	α S2-CN	f (	13 - 18	) SIIsQE
8	α S2-CN	f (	13 - 19	) SIIsQET
9	α S2-CN	f (	14 - 19	) IIsQET
10	α S2-CN	f (	23 - 35	) EKNMAINPsKENL
11	α S2-CN	f (	25 - 35	) NMAINPsKENL
12	α S2-CN	f (	25 - 35	) NmAINPsKENL
13	α S2-CN	f (	26 - 35	) MAINPsKENL
14	α S2-CN	f (	27 - 35	) AINPsKENL
15	α S2-CN	f (	28 - 33	) INPsKE
16	α S2-CN	f (	29 - 35	) NPsKENL
17	α S2-CN	f (	61 - 69	) sAEVATEEV
18	α S2-CN	f (	64 - 69	) VAtEEV
19	α S2-CN	f (	64 - 70	) VAtEEVK
20	α S2-CN	f (	124 - 133	) NREQLsTsEE
21	α S2-CN	f (	124 - 134	) NREQLsTsEEN
22	α S2-CN	f (	124 - 135	) NREQLsTSEENS
23	α S2-CN	f (	124 - 135	) NREQLsTsEENS
24	α S2-CN	f (	124 - 136	) NREQLsTSEENSK
25	α S2-CN	f (	124 - 136	) NREQLSTsEENSK
26	α S2-CN	f (	124 - 136	) NREQLsTsEENSK
27	α S2-CN	f (	124 - 136	) NREQLsTsEEEnSK
28	α S2-CN	f (	124 - 137	) NREQLSTsEENSKK
29	α S2-CN	f (	124 - 136	) NREQLsTsEENsK
30	α S2-CN	f (	124 - 137	) NREQLsTsEENSKK
31	α S2-CN	f (	124 - 137	) NREQLsTsEEEnSKK
32	α S2-CN	f (	124 - 137	) NREQLsTsEENsKK
33	α S2-CN	f (	124 - 138	) NREQLsTsEENSKKT
34	α S2-CN	f (	125 - 136	) REQLsTsEENSK
35	α S2-CN	f (	125 - 137	) REQLsTsEENSKK
36	α S2-CN	f (	126 - 136	) EQLSTsEENSK
37	α S2-CN	f (	126 - 136	) EQLsTsEENSK
38	α S2-CN	f (	126 - 136	) EQLsTsEENSK
39	α S2-CN	f (	126 - 137	) EQLSTsEENSKK
40	α S2-CN	f (	126 - 137	) EQLsTsEENSKK
41	α S2-CN	f (	126 - 137	) EQLsTsEEEnSKK
42	α S2-CN	f (	127 - 136	) QLsTsEENSK
43	α S2-CN	f (	127 - 137	) QLsTsEENSKK
44	α S2-CN	f (	128 - 136	) LSTsEENSK
45	α S2-CN	f (	128 - 136	) LsTsEENSK
46	α S2-CN	f (	128 - 137	) LSTsEENSKK
47	α S2-CN	f (	128 - 137	) LsTsEENSKK
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2	α S2-CN	f (	131 - 136	) sEENSK
3	α S2-CN	f (	137 - 145	) KTVDMesTE
4	α S2-CN	f (	137 - 146	) KTVDMesTEV
5	α S2-CN	f (	137 - 146	) KTVDMesTEV
6	α S2-CN	f (	137 - 147	) KTVDMesTEVF
7	α S2-CN	f (	137 - 147	) KTVDMesTEVF
8	α S2-CN	f (	137 - 147	) KTVDMesTEVF
9	α S2-CN	f (	137 - 148	) KTVDMesTEVFT
10	α S2-CN	f (	138 - 144	) TVDMesT
11	α S2-CN	f (	138 - 145	) TVDMesTE
12	α S2-CN	f (	138 - 146	) TVDMesTEV
13	α S2-CN	f (	138 - 146	) TVDMesTEV
14	α S2-CN	f (	138 - 146	) TVDMesTEV
15	α S2-CN	f (	138 - 146	) TVDMesTEV
16	α S2-CN	f (	138 - 147	) TVDMesTEVF
17	α S2-CN	f (	138 - 147	) TVDMesTEVF
18	α S2-CN	f (	138 - 147	) TVDMesTEVF
19	α S2-CN	f (	138 - 147	) TVDMesTEVF
20	α S2-CN	f (	138 - 148	) TVDMesTEVFT
21	α S2-CN	f (	138 - 148	) TVDMesTEVFT
22	α S2-CN	f (	138 - 148	) TVDMesTEVFT
23	α S2-CN	f (	138 - 148	) TVDMesTEVFT
24	α S2-CN	f (	138 - 149	) TVDMesTEVFTK
25	α S2-CN	f (	138 - 149	) TVDMesTEVFTK
26	α S2-CN	f (	138 - 150	) TVDMesTEVFTKK
27	α S2-CN	f (	138 - 150	) TVDMesTEVFTKK
28	α S2-CN	f (	139 - 146	) VDMesTEV
29	α S2-CN	f (	140 - 146	) DMEsTEV
30	α S2-CN	f (	140 - 147	) DMEsTEVF
31	α S2-CN	f (	140 - 148	) DMEsTEVFT
32	α S2-CN	f (	140 - 148	) DMEsTEVFT
33	α S2-CN	f (	141 - 146	) MEsTEV
34	α S2-CN	f (	141 - 147	) MEsTEVF
35	α S2-CN	f (	141 - 148	) MEsTEVFT
36	α S2-CN	f (	142 - 147	) EsTEVF
37	α S2-CN	f (	142 - 148	) EsTEVFT
38	β -CN	f (	1 - 16	) REELNVPGEIVeSL
39	β -CN	f (	3 - 16	) LEELNVPGEIVeSL
40	β -CN	f (	4 - 16	) EELNVPGEIVeSL
41	β -CN	f (	6 - 16	) LNVPGEIVeSL
42	β -CN	f (	7 - 16	) NVPGEIVeSL
43	β -CN	f (	8 - 16	) VPGEIVeSL
44	β -CN	f (	9 - 16	) PGEIVeSL
45	β -CN	f (	10 - 16	) GEIVeSL
46	β -CN	f (	11 - 16	) EIVeSL
47	β -CN	f (	15 - 25	) LSsssEESITR
48	β -CN	f (	16 - 22	) LSsssEES
49	β -CN	f (	16 - 22	) LsssEES
50	β -CN	f (	16 - 24	) LSsssEESIT
51	β -CN	f (	16 - 24	) LsssEESIT
52	β -CN	f (	16 - 24	) LsssEESIT
53	β -CN	f (	16 - 24	) LsssEESIT
54	β -CN	f (	16 - 24	) LsssEESIT
55	β -CN	f (	16 - 24	) LsssEESIT
56	β -CN	f (	16 - 24	) LsssEESIT
57	β -CN	f (	16 - 24	) LsssEESIT
58	β -CN	f (	16 - 24	) LsssEESIT
59	β -CN	f (	16 - 24	) LsssEESIT
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2	β -CN	f (	16 - 25	) LsssEESITR
3	β -CN	f (	16 - 26	) LsssEESITRI
4	β -CN	f (	17 - 22	) ssSEES
5	β -CN	f (	17 - 24	) SssEESIT
6	β -CN	f (	17 - 24	) sssEESIT
7	β -CN	f (	17 - 25	) sssEESITR
8	β -CN	f (	18 - 24	) sSEESIT
9	β -CN	f (	18 - 24	) SsEESIT
10	β -CN	f (	18 - 24	) ssEESIT
11	β -CN	f (	19 - 24	) sEESIT
12	β -CN	f (	29 - 45	) KIEKFqsEEQQQTEDEL
13	β -CN	f (	30 - 36	) IEKFQsE
14	β -CN	f (	30 - 37	) IEKFQsEE
15	β -CN	f (	30 - 38	) IEKFQsEEQ
16	β -CN	f (	30 - 39	) IEKFQsEEQQ
17	β -CN	f (	30 - 40	) IEKFQsEEQQQ
18	β -CN	f (	30 - 40	) IEKFqsEEQQQ
19	β -CN	f (	30 - 41	) IEKFQsEEQQQT
20	β -CN	f (	30 - 42	) IEKFQsEEQQQTE
21	β -CN	f (	30 - 43	) IEKFQsEEQQQTED
22	β -CN	f (	30 - 44	) IEKFQsEEQQQTEDE
23	β -CN	f (	30 - 44	) IEKFQsEEQQqTEDE
24	β -CN	f (	30 - 45	) IEKFQsEEQQQTEDEL
25	β -CN	f (	30 - 45	) IEKFQsEEqQQTEDEL
26	β -CN	f (	30 - 46	) IEKFQsEEQQQTEDELQ
27	β -CN	f (	30 - 47	) IEKFQsEEQQQTEDELQD
28	β -CN	f (	30 - 48	) IEKFQsEEQQQTEDELQDK
29	β -CN	f (	30 - 51	) IEKFQsEEQQQTEDELQDKIHP
30	β -CN	f (	30 - 52	) IEKFQsEEQQQTEDELQDKIHPP
31	β -CN	f (	31 - 36	) EKfQsE
32	β -CN	f (	31 - 44	) EKfQsEEQQQTEDE
33	β -CN	f (	31 - 45	) EKfQsEEQQQTEDEL
34	β -CN	f (	32 - 39	) KFQsEEQQ
35	β -CN	f (	32 - 40	) KFQsEEQQQ
36	β -CN	f (	32 - 42	) KFQsEEQQQTE
37	β -CN	f (	32 - 43	) KFQsEEQQQTED
38	β -CN	f (	32 - 44	) KFQsEEQQQTEDE
39	β -CN	f (	32 - 45	) KFQsEEQQQTEDEL
40	β -CN	f (	32 - 46	) KFQsEEQQQTEDELQ
41	β -CN	f (	32 - 48	) KFQsEEQQQTEDELQDK
42	β -CN	f (	33 - 38	) FQsEEQ
43	β -CN	f (	33 - 39	) FQsEEQQ
44	β -CN	f (	33 - 40	) FQsEEQQQ
45	β -CN	f (	33 - 41	) FQsEEQQQT
46	β -CN	f (	33 - 42	) FQsEEQQQTE

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2	β -CN	f (	33 - 42	) FQsEEQqQTE
3	β -CN	f (	33 - 43	) FQsEEQQQTED
4	β -CN	f (	33 - 44	) FQsEEQQQTEDE
5	β -CN	f (	33 - 44	) FQsEEQQQTEDE
6	β -CN	f (	33 - 44	) FQsEEQQqTEDE
7	β -CN	f (	33 - 45	) FQsEEQQQTEDEL
8	β -CN	f (	33 - 45	) FQsEEqQQTEDEL
9	β -CN	f (	33 - 46	) FQsEEQQQTEDELQ
10	β -CN	f (	33 - 47	) FQsEEQQQTEDELQD
11	β -CN	f (	33 - 48	) FQsEEQQQTEDELQDK
12	β -CN	f (	33 - 48	) FQsEEQQQTEDELQDK
13	β -CN	f (	33 - 48	) FQsEEqQQTEDELQDK
14	β -CN	f (	33 - 51	) FQsEEQQQTEDELQDKIHP
15	β -CN	f (	33 - 52	) FQsEEQQQTEDELQDKIHPF
16	β -CN	f (	34 - 43	) QsEEQqQTED
17	β -CN	f (	34 - 44	) QsEEQQQTEDE
18	β -CN	f (	34 - 45	) QsEEQQQTEDEL
19	β -CN	f (	34 - 46	) QsEEQQQTEDELQ
20	β -CN	f (	34 - 48	) QsEEQQQTEDELQDK
21	β -CN	f (	34 - 52	) QsEEQQQTEDELQDKIHPF
22	β -CN	f (	35 - 44	) sEEQQQTEDE
23	β -CN	f (	35 - 46	) sEEQQQTEDELQ
24	β -CN	f (	35 - 48	) sEEQQQTEDELQDK
25	β -CN	f (	35 - 52	) sEEQQQTEDELQDKIHPF
26	β -CN	f (	120 - 126	) TEsQSLT
27	β -CN	f (	121 - 126	) EsqSLT
28	κ -CN	f (	146 - 161	) LEDsPEVIESPPEINT
29	κ -CN	f (	147 - 153	) EDsPEVI
30	κ -CN	f (	147 - 160	) EDsPEVIESPPEIN
31	κ -CN	f (	147 - 161	) EDsPEVIESPPEINT
32	κ -CN	f (	149 - 169	) sPEVIESPPEINTVQVTSTAV
33	κ -CN	f (	153 - 165	) IESPPEINTVqVt
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2 d extract of digesta of **Trentingrana (TN)** at **13 months** of ripening [digestion according the **PePan** protocol]
3 ith CaCl₂ at pH value of:
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Modifications	MH+ [Da]	Delta Mass [PPM]	RT [min]	Color code
S7(Phospho)	1026.486	-0.30	4.8	b
S7(Phospho); S12(Phospho); S14(Phospho)	2004.744	-2.33	8.7	r
S7(Phospho); S12(Phospho)	2167.868	-0.04	8.9	r
S7(Phospho); S12(Phospho); S14(Phospho)	2247.835	0.28	8.5	r
S7(Phospho); S12(Phospho); S14(Phospho)	2693.982	0.25	10.2	r
S6(Phospho); S11(Phospho); S13(Phospho)	2118.791	-0.23	8.2	r
S6(Phospho); S11(Phospho); S13(Phospho)	2564.939	-0.07	10.0	r
S5(Phospho)	769.349	-0.81	4.1	b
N2(Deamidated); S5(Phospho)	1055.466	0.74	9.5	n
S5(Phospho); S10(Phospho)	1350.523	-0.10	8.9	r
S5(Phospho); S10(Phospho)	1910.730	-0.24	8.9	n
S12(Phospho); T13(Phospho)	1910.730	-0.05	8.4	r
S5(Phospho); S10(Phospho); S12(Phospho)	1990.697	-0.06	12.3	r
S5(Phospho); S10(Phospho); S12(Phospho)	2061.733	-0.36	9.0	r
S5(Phospho); S10(Phospho); S12(Phospho)	2192.774	-0.10	11.2	r
S5(Phospho); S10(Phospho); S12(Phospho)	2436.844	-0.08	11.2	r
S10(Phospho); T11(Phospho)	1697.617	-0.97	7.2	n
S8(Phospho); S10(Phospho)	1697.619	-0.26	7.0	r
S8(Phospho); S10(Phospho)	2143.764	-0.98	9.4	r
S7(Phospho); S9(Phospho)	1325.490	-0.64	6.4	r
S7(Phospho); S9(Phospho)	1440.517	-0.48	6.4	r
S9(Phospho)	1488.609	-0.52	6.4	n
S7(Phospho)	1488.610	0.13	6.6	r
S7(Phospho); S9(Phospho)	1568.575	-1.29	6.3	b
S7(Phospho); S9(Phospho)	1639.613	-0.12	7.1	b
S2(Phospho); S7(Phospho); S9(Phospho)	1648.542	-0.50	6.0	r
S7(Phospho); S9(Phospho)	1770.654	-0.03	8.4	r
S7(Phospho); S9(Phospho)	1899.696	-0.48	8.2	r
S7(Phospho); S9(Phospho); M15(Oxidation)	1915.692	0.02	7.1	r
S7(Phospho); S9(Phospho)	2014.723	-0.37	8.2	r
S9(Phospho); T10(Phospho)	2255.903	0.06	11.5	r
S7(Phospho); S9(Phospho)	2383.961	0.06	11.4	r
S7(Phospho); S9(Phospho)	2515.002	0.17	14.6	r
S6(Phospho); S8(Phospho)	1212.406	-0.73	3.4	r
S6(Phospho)	1375.527	0.29	4.0	b
S6(Phospho); S8(Phospho)	1455.493	0.35	4.3	b
S6(Phospho); S8(Phospho)	1526.529	-0.64	5.3	b

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2	S6(Phospho); S8(Phospho)	1657.569	-0.64	7.1 b
3	S6(Phospho); S8(Phospho)	1786.609	-2.24	7.0 b
4	S6(Phospho); S8(Phospho); M14(Oxidation)	1802.607	-0.34	5.6 r
5	S6(Phospho); S8(Phospho)	1901.639	-0.10	7.9 r
6	S6(Phospho); S8(Phospho); M14(Oxidation)	1917.633	-0.88	5.7 r
7	S8(Phospho); T9(Phospho)	2014.723	-0.13	12.3 r
8	S6(Phospho); S8(Phospho)	2142.817	-0.69	10.9 b
9	S6(Phospho); S8(Phospho)	2270.877	-0.22	10.8 b
10	S6(Phospho); S8(Phospho)	2401.918	-0.09	14.2 b
11	S6(Phospho); S8(Phospho)	2530.961	0.44	14.5 r
12	S6(Phospho); S8(Phospho)	2731.043	0.99	15.2 r
13	S5(Phospho); S7(Phospho)	1368.459	-0.76	3.5 r
14	S5(Phospho); S7(Phospho)	1439.497	-0.47	5.3 r
15	S5(Phospho); S7(Phospho)	1814.607	-0.34	7.8 r
16	S5(Phospho); S7(Phospho)	2055.786	-0.11	11.0 r
17	S4(Phospho); S6(Phospho)	997.279	-0.88	4.2 r
18	S4(Phospho)	1160.400	0.81	5.2 b
19	S4(Phospho); S6(Phospho)	1240.365	-0.68	4.9 r
20	S4(Phospho); S6(Phospho)	1311.402	-0.24	6.1 r
21	S4(Phospho); S6(Phospho); M12(Oxidation)	1587.480	-0.67	6.5 r
22	T7(Phospho)	1606.546	-0.15	8.4 r
23	S4(Phospho); S6(Phospho)	1686.514	0.93	17.4 r
24	S4(Phospho)	1847.725	-0.17	11.5 n
25	S4(Phospho); S6(Phospho)	1927.689	-1.19	11.9 b
26	S4(Phospho); S6(Phospho); M12(Oxidation)	1943.686	-0.20	9.0 r
27	S4(Phospho)	1975.785	0.46	11.4 n
28	S4(Phospho); S6(Phospho)	2055.750	-0.10	11.8 b
29	S4(Phospho); S6(Phospho); M12(Oxidation)	2071.750	2.12	9.1
30	S4(Phospho); S6(Phospho)	2186.790	-0.19	15.2 b
31	S4(Phospho); S6(Phospho); M12(Oxidation)	2202.786	0.12	12.4 r
32	S4(Phospho); S6(Phospho)	2315.835	0.50	15.3 r
33	S4(Phospho); S6(Phospho); M12(Oxidation)	2331.829	0.48	12.9 r
34	S4(Phospho); S6(Phospho)	2515.913	-0.17	16.1 r
35	S3(Phospho); S5(Phospho)	1125.338	-0.77	3.0 r
36	S3(Phospho); S5(Phospho)	1812.665	0.07	11.2 r
37	S2(Phospho); S4(Phospho)	1012.254	-0.17	4.6 r
38	S1(Phospho); S3(Phospho)	955.234	0.96	2.0 r
39	T4(Phospho)	1077.344	-0.02	5.2 n
40	S8(Phospho)	1128.501	-0.16	9.7 b
41	S6(Phospho)	887.322	0.67	8.6 b
42	S5(Phospho)	759.263	0.52	8.5 n
43	S2(Phospho); S3(Phospho); S4(Phospho)	1314.432	1.42	17.6 r
44	S1(Phospho)	954.382	0.54	8.5 b
45	S1(Phospho); S2(Phospho)	1034.348	0.30	8.4 b
46	S2(Phospho); S9(Phospho)	1605.644	-0.21	9.0 b
47	S1(Phospho); S2(Phospho); S9(Phospho)	1685.610	-0.29	8.7 r
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2	S1(Phospho)	867.349	-0.90	8.6 n
3	S6(Phospho)	1222.572	0.02	8.5 n
4	S7(Phospho)	1351.615	0.47	9.1 n
5	S3(Phospho)	881.377	0.06	8.9 n
6	Q3(Deamidated)	1338.665	0.16	5.2 n
7	S9(Phospho)	1417.648	0.40	5.1 n
8	S12(Phospho)	1537.766	-0.05	15.3 n
9	S12(Phospho)	1795.851	-0.25	15.1 n
10	S12(Phospho)	1951.953	0.13	14.4 n
11	S11(Phospho)	1374.702	-0.71	14.0 n
12	S11(Phospho)	1632.786	-1.11	13.9 n
13	S11(Phospho)	1788.889	-0.36	13.0 n
14	S10(Phospho)	1660.793	-0.76	13.5 n
15	S8(Phospho)	1464.673	-0.13	11.5 n
16	Q1(Deamidated); S8(Phospho)	1465.657	0.12	11.8 n
17	S7(Phospho)	922.428	0.04	11.8 b
18	S7(Phospho)	1180.515	1.11	11.7 b
19	S7(Phospho)	1336.613	-0.97	11.0 b
20	N6(Deamidated); S7(Phospho)	1337.598	-0.61	11.6 b
21	S7(Phospho)	1449.699	0.39	14.5 n
22	N6(Deamidated); S7(Phospho)	1450.683	0.56	14.7 n
23	S7(Phospho)	1586.757	-0.15	12.5 b
24	S6(Phospho)	809.343	-1.05	8.1 b
25	N5(Deamidated); S6(Phospho)	810.328	-0.15	8.7 n
26	S6(Phospho)	938.385	-1.55	7.8 n
27	S6(Phospho)	1067.429	-0.29	8.1 b
28	N5(Deamidated); S6(Phospho)	1068.413	-0.57	8.7 b
29	S6(Phospho)	1223.529	-0.79	7.6 b
30	N5(Deamidated); S6(Phospho)	1224.515	0.50	8.0 b
31	S6(Phospho)	1336.614	-0.24	11.9 b
32	N5(Deamidated); S6(Phospho)	1337.597	-1.34	12.3 n
33	S6(Phospho)	1473.673	-0.35	9.9 b
34	N5(Deamidated); S6(Phospho)	1474.657	-0.27	10.3 n
35	S6(Phospho)	1691.745	-0.60	12.4 r
36	S5(Phospho)	1094.487	-0.44	5.7 b
37	N4(Deamidated); S5(Phospho)	1095.470	-1.56	6.1 n
38	S4(Phospho)	981.403	-1.01	7.6 b
39	N3(Deamidated); S4(Phospho)	982.387	-1.26	8.0 b
40	S3(Phospho)	726.234	-0.97	8.1 b
41	S3(Phospho)	882.335	-0.78	7.5 b
42	N2(Deamidated); S3(Phospho)	883.318	-1.68	8.0 b
43	S3(Phospho)	995.418	-1.08	11.9 n
44	S3(Phospho)	1132.478	-0.43	9.9 b
45	S2(Phospho)	1345.566	-4.42	6.8 b
46	S6(Phospho)	880.312	-0.51	10.5 b
47	S5(Phospho)	717.249	-0.59	9.3 b
48	S9(Phospho)	1566.668	-0.08	11.0 n
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2	T15(Phospho)	2109.941	0.17	15.5 n
3	S8(Phospho); S9(Phospho); S10(Phospho)	1617.493	-0.65	5.3 r
4	S10(Phospho); S13(Phospho); S16(Phospho)	2375.875	-0.06	11.2 r
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6	S2(Phospho); S3(Phospho); S4(Phospho)	964.198	-0.41	4.0 r
7	S1(Phospho); S2(Phospho)	785.164	0.07	2.4 r
8	S4(Phospho)	756.317	-0.22	9.3 n
9	S4(Phospho)	857.364	-0.99	10.0 n
10	S3(Phospho)	770.333	-0.57	7.0 n
11	S9(Phospho)	1567.718	-0.30	10.4 n
12	S7(Phospho)	1310.581	0.10	11.4 n
13	M2(Oxidation); S7(Phospho)	1326.576	0.34	9.4 n
14	S6(Phospho)	1196.538	-0.23	11.2 n
15	S5(Phospho)	1065.499	1.09	8.9 n
16	S4(Phospho)	767.333	-0.62	2.6 n
17	S3(Phospho)	881.377	0.06	8.9 n
18	S1(Phospho)	1014.404	0.79	8.6 n
19	T3(Phospho)	727.290	-0.75	6.5 n
20	T3(Phospho)	855.385	-0.71	4.8 n
21	S6(Phospho); S8(Phospho)	1352.476	-0.55	5.2 r
22	S6(Phospho); S8(Phospho)	1466.519	-0.31	4.3 r
23	S6(Phospho)	1473.586	0.08	5.0 n
24	S6(Phospho); S8(Phospho)	1553.552	0.38	4.6 b
25	S6(Phospho)	1601.679	-1.14	4.4 n
26	S8(Phospho)	1601.679	-0.68	4.7 r
27	S6(Phospho); S8(Phospho)	1681.645	-0.74	4.4 b
28	S6(Phospho); S8(Phospho); N11(Deamidated)	1682.631	0.06	3.9 b
29	S8(Phospho)	1729.773	-1.41	3.6 r
30	S6(Phospho); S8(Phospho); S12(Phospho)	1761.611	-0.99	3.4 r
31	S6(Phospho); S8(Phospho)	1809.741	-0.15	3.4 b
32	S6(Phospho); S8(Phospho); N11(Deamidated)	1810.724	-0.76	3.3 b
33	S6(Phospho); S8(Phospho); S12(Phospho)	1889.706	-1.06	3.0 r
34	S6(Phospho); S8(Phospho)	1910.787	-1.01	4.3 b
35	S5(Phospho); S7(Phospho)	1567.602	-0.82	4.2 b
36	S5(Phospho); S7(Phospho)	1695.697	-1.26	3.4 r
37	S6(Phospho)	1331.537	0.19	4.7 b
38	S4(Phospho); S6(Phospho)	1411.502	-0.53	3.8 r
39	S4(Phospho); S6(Phospho)	1411.502	-0.18	3.9 n
40	S6(Phospho)	1459.630	-0.75	3.8 b
41	S4(Phospho); S6(Phospho)	1539.596	-0.80	3.3 b
42	S4(Phospho); S6(Phospho); N9(Deamidated)	1540.581	-0.49	4.0 r
43	S3(Phospho); S5(Phospho)	1282.460	-0.11	2.8 r
44	S3(Phospho); S5(Phospho)	1410.555	0.08	2.6 r
45	S4(Phospho)	1074.436	1.02	2.8 n
46	S2(Phospho); S4(Phospho)	1154.402	0.19	2.5 r
47	S4(Phospho)	1202.531	0.40	2.3 n
48	S2(Phospho); S4(Phospho)	1282.497	0.64	2.3 b
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2	S1(Phospho)	773.271	-0.75	4.3 r
3	S7(Phospho)	1119.428	0.05	6.2 n
4	S7(Phospho)	1218.495	-0.80	9.2 b
5	M5(Oxidation); S7(Phospho)	1234.491	-0.23	6.5 n
6	T8(Phospho)	1365.564	-0.58	13.2 n
8	S7(Phospho)	1365.565	0.04	13.2 r
9	S7(Phospho)	1466.611	-0.68	12.3 b
10	S6(Phospho)	862.290	-0.06	6.1 b
11	S6(Phospho)	991.333	0.32	6.3 b
12	S6(Phospho)	1090.400	-0.68	9.6 n
13	T7(Phospho)	1090.401	0.06	9.6 r
14	M4(Oxidation); S6(Phospho)	1106.396	0.07	6.7 b
15	T7(Phospho)	1237.468	-0.84	13.8 n
16	S6(Phospho)	1237.469	-0.15	13.7 r
17	M4(Oxidation); S6(Phospho)	1253.465	0.46	11.4 n
18	S6(Phospho)	1338.518	0.59	12.8 n
19	T7(Phospho)	1338.519	1.32	12.8 r
20	M4(Oxidation); S6(Phospho)	1354.513	0.46	10.5 n
21	T7(Phospho)	1466.611	-0.76	12.0 n
22	S6(Phospho)	1466.612	-0.18	12.0 r
23	T7(Phospho)	1594.706	-0.77	11.2 n
24	S6(Phospho)	1594.707	0.22	11.2 r
25	S5(Phospho)	989.353	-0.35	9.4 n
26	S4(Phospho)	890.284	-0.87	8.0 b
27	S4(Phospho)	1037.352	-1.27	12.9 b
28	T5(Phospho)	1138.401	0.17	11.8 r
29	S4(Phospho)	1138.401	0.38	11.8 n
30	S3(Phospho)	775.257	-0.72	6.4 b
31	S3(Phospho)	922.326	-0.40	11.9 b
32	S3(Phospho)	1023.373	-0.67	10.9 b
33	S2(Phospho)	791.286	0.03	10.5 n
34	S2(Phospho)	892.334	0.22	9.4 b
35	S15(Phospho)	1905.923	1.140	17.4 b
36	S13(Phospho)	1620.778	0.76	17.67 b
37	S12(Phospho)	1507.693	-0.02	16.57 b
38	S10(Phospho)	1249.609	0.95	16.12 b
39	S9(Phospho)	1136.523	-0.27	14.06 b
40	S8(Phospho)	1022.479	-1.4	13.6 n
41	S7(Phospho)	923.4122	-0.03	16.48 b
42	S6(Phospho)	826.3578	-1.99	12.24 n
43	S5(Phospho)	769.3375	-0.57	11.73 n
44	S3(Phospho); S4(Phospho); S5(Phospho)	1435.479	0.2	7.96 r
45	S3(Phospho); S4(Phospho)	898.2484	0.58	2.00 r
46	S2(Phospho); S3(Phospho); S4(Phospho)	978.2146	0.38	11.21 r
47	S3(Phospho); S4(Phospho)	1112.38	0	7.36 r
48	S2(Phospho); S3(Phospho); S4(Phospho)	1192.347	1.1	16.62 r
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S2(Phospho); S3(Phospho); S4(Phospho)	1348.447	0.25	7.22 r
S2(Phospho); S3(Phospho); S4(Phospho)	1461.531	-0.16	12.07 r
S1(Phospho); S2(Phospho)	785.1639	0.07	2.43 r
S2(Phospho); S3(Phospho)	999.2956	0.02	5.52 n
S1(Phospho); S2(Phospho); S3(Phospho)	1079.262	0.05	9.98 r
S1(Phospho); S2(Phospho); S3(Phospho)	1235.362	-0.54	4.92 r
S1(Phospho)	832.2965	-0.92	5.32 n
S2(Phospho)	832.2966	-0.77	5.31 r
S1(Phospho); S2(Phospho)	912.2632	-0.39	5.35 b
S1(Phospho)	745.2643	-1.13	5.32 n
Q6(Deamidated); S7(Phospho)	2189.949	-0.06	10.88 n
S6(Phospho)	960.4066	-0.92	6.82 n
S6(Phospho)	1089.45	-0.49	7.21 b
S6(Phospho)	1217.508	-0.83	6.86 b
S6(Phospho)	1345.565	-2.01	6.93 b
S6(Phospho)	1473.624	-1	6.85 b
Q5(Deamidated); S6(Phospho)	1474.609	-0.34	7.25 n
S6(Phospho)	1574.672	-0.67	7.26 b
S6(Phospho)	1703.715	-0.4	7.4 b
S6(Phospho)	1818.742	-0.76	7.45 b
S6(Phospho)	1947.784	-0.9	8.07 b
S6(Phospho); Q11(Deamidated)	1948.773	1.48	8.25 b
S6(Phospho)	2060.87	0.12	11.29 b
Q5(Deamidated); S6(Phospho)	2061.854	0.05	11.41 r
S6(Phospho); Q9(Deamidated)	2061.86	3.13	11.37 n
S6(Phospho)	2188.928	-0.11	9.34 b
S6(Phospho)	2303.954	-0.36	9.37 b
S6(Phospho)	2432.048	-0.94	9.91 b
S6(Phospho)	2779.242	-1.33	12.24 n
S6(Phospho)	2926.311	-1.2	14.55 b
S5(Phospho)	847.3229	-0.51	6.83 n
S5(Phospho)	1834.7	-0.84	6.64 b
S5(Phospho)	1947.785	-0.52	10.23 n
S4(Phospho)	1103.44	-0.05	3.55 n
S4(Phospho)	1231.498	-0.63	3.75 n
S4(Phospho)	1461.589	-0.24	5.25 n
S4(Phospho)	1576.617	0.57	5.4 n
S4(Phospho)	1705.658	-0.62	5.98 b
S4(Phospho)	1818.741	-1.03	9.95 b
S4(Phospho)	1946.802	0.3	9.05 n
S4(Phospho)	2189.924	0.05	8.99 n
S3(Phospho)	847.2872	0.29	2.9 b
S3(Phospho)	975.3446	-0.98	3.01 b
S3(Phospho)	1103.403	-0.81	3.08 b
S3(Phospho)	1204.452	-0.2	4.35 n
S3(Phospho)	1333.493	-1	4.72 b

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2	S3(Phospho); Q7(Deamidated)	1334.478	0	5.17 n
3	S3(Phospho)	1448.52	-0.82	4.92 b
4	S3(Phospho)	1577.562	-0.98	5.68 b
5	Q2(Deamidated); S3(Phospho)	1578.548	-0.13	6.38 r
6	S3(Phospho); Q8(Deamidated)	1578.551	2.11	6.14 n
7	S3(Phospho)	1690.647	-0.68	10.34 b
8	S3(Phospho); Q6(Deamidated)	1691.639	4.37	10.54 b
9	S3(Phospho)	1818.704	-1.23	7.87 b
10	S3(Phospho)	1933.733	-0.38	9.18 b
11	S3(Phospho)	2061.83	0.77	8.43 b
12	Q2(Deamidated); S3(Phospho)	2062.813	-0.01	9.97 n
13	S3(Phospho); Q6(Deamidated)	2062.814	0.59	9.83 r
14	S3(Phospho)	2409.022	-1.15	12.22 b
15	S3(Phospho)	2556.092	-0.24	15.05 b
16	S2(Phospho); Q7(Deamidated)	1302.438	0.82	2.01 r
17	S2(Phospho)	1430.495	-0.61	2.21 b
18	S2(Phospho)	1543.579	-0.39	8.30 r
19	S2(Phospho)	1543.581	0.72	8.38 n
20	S2(Phospho)	1671.637	-0.79	7.18 n
21	S2(Phospho)	1914.758	-1.05	7.23 b
22	S2(Phospho)	2409.022	-0.94	14.11 n
23	S1(Phospho)	1302.438	0.82	2.01 r
24	S1(Phospho)	1543.579	-0.54	8.29 b
25	S1(Phospho)	1786.699	-1.27	7.16 b
26	S1(Phospho)	2280.961	-1.86	14.15 n
27	S3(Phospho)	845.3292	0.45	5.11 n
28	S2(Phospho); Q3(Deamidated)	745.2643	-1.12	5.32 n
29	S4(Phospho)	1848.815	0.05	13.4 n
30	S3(Phospho)	868.333	-1.19	9.9 n
31	S3(Phospho)	1634.682	-0.66	12.5 n
32	S3(Phospho)	1735.732	0.32	12.8 b
33	S1(Phospho)	2277.089	-0.52	15.5 n
34	Q11(Deamidated); T13(Phospho)	1507.693	-0.09	16.5 b
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Number of phosphorylated serine residues per peptide	Number of phosphorylated threonine residues per peptide	Number of phosphorylated residues per peptides
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2	0	2

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Peptide length	Max peptide length	Min peptide length
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For Peer Review

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For Peer Review

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For Peer Review

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Supplementary Table S1. TN_19. Caseinophosphopeptides identified in enriched CPPs isolated from cheese digesta by selective precipitation with pH 8.0 are indicated in black; pH 4.6 are indicated in red; both, pH 8.0 and pH 4.6, are indicated in blue.

Protein fragment			Sequence
α S1-CN	f (	35 - 42	) EKVNELsK
α S1-CN	f (	35 - 52	) EKVNELsKDIGsEsTEDQ
α S1-CN	f (	35 - 54	) EKVNELsKDIGsEsTEDQAM
α S1-CN	f (	35 - 55	) EKVNELsKDIGsEsTEDQAME
α S1-CN	f (	35 - 56	) EKVNELsKDIGsEsTEDQAMED
α S1-CN	f (	36 - 55	) KVNELsKDIGsEsTEDQAME
α S1-CN	f (	37 - 42	) VNELsK
α S1-CN	f (	37 - 45	) VnELsKDIG
α S1-CN	f (	37 - 47	) VNELsKDIGsE
α S1-CN	f (	37 - 50	) VNELsKDIGsEsTE
α S1-CN	f (	37 - 51	) VNELsKDIGsEsTED
α S1-CN	f (	37 - 52	) VNELSKDIGSEstEDQ
α S1-CN	f (	37 - 52	) VnELSKDIGsEsTEDQ
α S1-CN	f (	37 - 52	) VNELsKDIGsEsTEDQ
α S1-CN	f (	37 - 53	) VNELsKDIGsEsTEDQA
α S1-CN	f (	37 - 54	) VNELsKDIGsEsTEDQAM
α S1-CN	f (	37 - 55	) VNELsKDIGsEsTEDQAME
α S1-CN	f (	37 - 55	) VNELsKDIGsEsTEDQAmE
α S1-CN	f (	37 - 56	) VNELsKDIGsEsTEDQAMED
α S1-CN	f (	37 - 58	) VNELsKDIGsEsTEDQAMEDIK
α S1-CN	f (	37 - 60	) VNELsKDIGsEsTEDQAMEDIKQM
α S1-CN	f (	38 - 52	) NELsKDIGsEsTEDQ
α S1-CN	f (	39 - 52	) ELsKDIGsEsTEDQ
α S1-CN	f (	39 - 52	) ELsKDIGsEsTEDQ
α S1-CN	f (	40 - 50	) LSKDIGsEsTE
α S1-CN	f (	40 - 51	) LSKDIGsEsTED
α S1-CN	f (	40 - 52	) LSKDIGSEstEDQ
α S1-CN	f (	40 - 52	) LSKDIGsEsTEDQ
α S1-CN	f (	40 - 52	) LSKDIGsEsTEDq
α S1-CN	f (	40 - 53	) LSKDIGsEsTEDQA
α S1-CN	f (	40 - 52	) LsKDIGsEsTEDQ
α S1-CN	f (	40 - 54	) LSKDIGsEsTEDQAM
α S1-CN	f (	40 - 54	) LSKDIGsEsTEDqAM
α S1-CN	f (	40 - 55	) LSKDIGsEsTEDQAME
α S1-CN	f (	40 - 55	) LSKDIGSEstEDqAME
α S1-CN	f (	40 - 55	) LSKDIGsEsTEDQAmE
α S1-CN	f (	40 - 56	) LSKDIGsEsTEDQAMED

1				
2	α S1-CN	f (	40 - 56	) LSKDIGsEsTEDqAMED
3	α S1-CN	f (	40 - 56	) LSKDIGsEsTEDQAmED
4	α S1-CN	f (	40 - 57	) LSKDIGsEsTEDQAMEDI
5	α S1-CN	f (	40 - 58	) LSKDIGsEsTEDQAMEDIK
6	α S1-CN	f (	40 - 59	) LSKDIGsEsTEDQAMEDIKQ
7	α S1-CN	f (	40 - 60	) LSKDIGsEsTEDQAMEDIKQM
8	α S1-CN	f (	40 - 61	) LSKDIGsEsTEDQAMEDIKQME
9	α S1-CN	f (	41 - 52	) SKDIGsESTEDQ
10	α S1-CN	f (	41 - 52	) SKDIGsEsTEDQ
11	α S1-CN	f (	41 - 53	) SKDIGsEsTEDQA
12	α S1-CN	f (	41 - 52	) sKDIGsEsTEDQ
13	α S1-CN	f (	41 - 54	) SKDIGsEsTEDQAM
14	α S1-CN	f (	41 - 55	) SKDIGSEstEDQAME
15	α S1-CN	f (	41 - 56	) SKDIGsEsTEDQAMED
16	α S1-CN	f (	41 - 58	) SKDIGsEsTEDQAMEDIK
17	α S1-CN	f (	41 - 59	) SKDIGsEsTEDQAMEDIKQ
18	α S1-CN	f (	41 - 60	) SKDIGsEsTEDQAMEDIKQM
19	α S1-CN	f (	41 - 61	) SKDIGSEstEDQAMEDIKQME
20	α S1-CN	f (	41 - 63	) SKDIGSEstEDQAMEDIKQMEAE
21	α S1-CN	f (	42 - 52	) KDIGsEsTEDQ
22	α S1-CN	f (	42 - 53	) KDIGsEsTEDQA
23	α S1-CN	f (	42 - 54	) KDIGsEsTEDQAM
24	α S1-CN	f (	42 - 56	) KDIGsEsTEDQAMED
25	α S1-CN	f (	43 - 50	) DIGSEstE
26	α S1-CN	f (	43 - 51	) DIGsEsTED
27	α S1-CN	f (	43 - 52	) DIGsESTEDQ
28	α S1-CN	f (	43 - 52	) DIGsEsTEDQ
29	α S1-CN	f (	43 - 53	) DIGsESTEDQA
30	α S1-CN	f (	43 - 53	) DIGsEsTEDQA
31	α S1-CN	f (	43 - 54	) DIGsEsTEDQAM
32	α S1-CN	f (	43 - 55	) DIGsEsTEDQAME
33	α S1-CN	f (	43 - 55	) DIGsEsTEDQAmE
34	α S1-CN	f (	43 - 56	) DIGsEsTEDQAMED
35	α S1-CN	f (	43 - 57	) DIGsEsTEDQAMEDI
36	α S1-CN	f (	43 - 58	) DIGsESTEDQAMEDIK
37	α S1-CN	f (	43 - 58	) DIGsEsTEDQAMEDIK
38	α S1-CN	f (	43 - 58	) DIGsEsTEDQAmEDIK
39	α S1-CN	f (	43 - 59	) DIGsEsTEDQAMEDIKQ
40	α S1-CN	f (	43 - 59	) DIGsEsTEDQAmEDIKQ
41	α S1-CN	f (	43 - 60	) DIGsEsTEDQAMEDIKQM
42	α S1-CN	f (	43 - 60	) DIGsEsTEDQAmEDIKQM
43	α S1-CN	f (	43 - 61	) DIGsEsTEDQAMEDIKQME
44	α S1-CN	f (	43 - 63	) DIGsEsTEDQAMEDIKQMEAE
45	α S1-CN	f (	44 - 52	) IGsEsTEDQ
46	α S1-CN	f (	44 - 58	) IGsEsTEDQAMEDIK
47	α S1-CN	f (	45 - 52	) GsEsTEDQ
48	α S1-CN	f (	57 - 65	) IKQMEAEsI
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2	α S1-CN	f (	59 - 65	) QMEAEsI
3	α S1-CN	f (	60 - 65	) MEAEsI
4	α S1-CN	f (	64 - 74	) sIssSEEIVPN
5	α S1-CN	f (	65 - 74	) IssSEEIVPN
6	α S1-CN	f (	65 - 74	) IsssEEIVPN
7	α S1-CN	f (	66 - 89	) SssEEIVPNsVEQK
8	α S1-CN	f (	67 - 74	) sSEEIVPN
9	α S1-CN	f (	67 - 74	) ssEEIVPN
10	α S1-CN	f (	67 - 79	) SsEEIVPNsVEQK
11	α S1-CN	f (	67 - 89	) ssEEIVPNsVEQK
12	α S1-CN	f (	69 - 79	) EEIVPNsVEQK
13	α S1-CN	f (	73 - 79	) PNsVEQK
14	α S1-CN	f (	96 - 78	) EIVPNsVEQK
15	α S1-CN	f (	104 - 116	) YKVPQLEIVPNsA
16	α S1-CN	f (	104 - 118	) YKVPQLEIVPNsAEE
17	α S1-CN	f (	104 - 119	) YKVPQLEIVPNsAEER
18	α S1-CN	f (	104 - 119	) YKVPQLEIVPnsAEER
19	α S1-CN	f (	105 - 116	) KVPQLEIVPNsA
20	α S1-CN	f (	105 - 118	) KVPQLEIVPNsAEE
21	α S1-CN	f (	105 - 119	) KVPQLEIVPNsAEER
22	α S1-CN	f (	105 - 119	) KVPQLEIVPnsAEER
23	α S1-CN	f (	106 - 119	) VPQLEIVPNsAEER
24	α S1-CN	f (	106 - 119	) VPQLEIVPnsAEER
25	α S1-CN	f (	109 - 116	) LEIVPNsA
26	α S1-CN	f (	109 - 118	) LEIVPNsAEE
27	α S1-CN	f (	109 - 119	) LEIVPNsAEER
28	α S1-CN	f (	109 - 119	) LEIVPnsAEER
29	α S1-CN	f (	110 - 116	) EIVPNsA
30	α S1-CN	f (	110 - 116	) EIVPnsA
31	α S1-CN	f (	110 - 117	) EIVPNsAE
32	α S1-CN	f (	110 - 118	) EIVPNsAEE
33	α S1-CN	f (	110 - 118	) EIVPnsAEE
34	α S1-CN	f (	110 - 119	) EIVPNsAEER
35	α S1-CN	f (	110 - 119	) EIVPnsAEER
36	α S1-CN	f (	110 - 120	) EIVPNsAEERL
37	α S1-CN	f (	110 - 121	) EIVPNsAEERLH
38	α S1-CN	f (	110 - 121	) EIVPnsAEERLH
39	α S1-CN	f (	111 - 119	) IVPNsAEER
40	α S1-CN	f (	111 - 119	) IVPnsAEER
41	α S1-CN	f (	112 - 119	) VPnsAEER
42	α S1-CN	f (	112 - 119	) VPnsAEER
43	α S1-CN	f (	113 - 118	) PNsAEE
44	α S1-CN	f (	113 - 118	) PnsAEE
45	α S1-CN	f (	113 - 119	) PNsAEER
46	α S1-CN	f (	113 - 121	) PnsAEERLH
47	α S1-CN	f (	121 - 131	) HsMKEGIHAQQ
48				
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2	α S1-CN	f (	173 - 179	) YTDAPsF
3	α S1-CN	f (	174 - 179	) TDAPsF
4	α S1-CN B	f (	180 - 193	) SDIPNPIGsENSEK
5	α S1-CN B	f (	180 - 198	) SDIPNPIGsENSEKtTMPL
6				
7	α S2-CN	f (	1 - 12	) KNTMEHVsssEE
8	α S2-CN	f (	1 - 19	) KNTMEHVSSsEEsIIsQET
9				
10	α S2-CN	f (	7 - 13	) VsssEES
11	α S2-CN	f (	8&56 - 13&61	) sssEES
12	α S2-CN	f (	9 - 15	) ssEESII
13	α S2-CN	f (	9 - 16	) ssEESIIS
14	α S2-CN	f (	9 - 18	) ssEEsIISQE
15				
16	α S2-CN	f (	13 - 18	) SIIsQE
17	α S2-CN	f (	13 - 19	) SIIsQET
18	α S2-CN	f (	14 - 19	) IIsQET
19				
20	α S2-CN	f (	23 - 35	) EKNMAINPsKENL
21	α S2-CN	f (	25 - 34	) NMAINPsKEN
22	α S2-CN	f (	25 - 35	) NMAINPsKENL
23	α S2-CN	f (	25 - 35	) nMAINPsKENL
24	α S2-CN	f (	25 - 35	) NmAINPsKENL
25	α S2-CN	f (	26 - 34	) MAINPsKEN
26	α S2-CN	f (	26 - 35	) MAINPsKENL
27	α S2-CN	f (	27 - 35	) AINPsKENL
28	α S2-CN	f (	27 - 35	) AInPsKENL
29	α S2-CN	f (	29 - 35	) NPsKENL
30	α S2-CN	f (	30 - 35	) PsKENL
31				
32	α S2-CN	f (	53 - 70	) SIGsssEEsAEVATEEVK
33	α S2-CN	f (	61 - 69	) sAEVATEEV
34	α S2-CN	f (	64 - 69	) VAtEEV
35				
36	α S2-CN	f (	67 - 76	) QLsTsEENSK
37	α S2-CN	f (	104 - 146	) DMEsTEV
38				
39	α S2-CN	f (	124 - 133	) NREQLsTsEE
40	α S2-CN	f (	124 - 134	) NREQLsTsEEN
41	α S2-CN	f (	124 - 135	) NREQLsTsEENS
42				
43	α S2-CN	f (	124 - 136	) NREQLSTsEENSK
44	α S2-CN	f (	124 - 136	) NREQLsTsEENSK
45	α S2-CN	f (	124 - 136	) NREQLsTsEEEnSK
46	α S2-CN	f (	124 - 137	) NREQLsTsEENSKK
47	α S2-CN	f (	124 - 137	) NREQLsTsEEEnSKK
48	α S2-CN	f (	124 - 137	) NREQLsTsEENsKK
49				
50	α S2-CN	f (	125 - 137	) REQLsTsEENSKK
51	α S2-CN	f (	126 - 136	) EQLsTSEENSK
52	α S2-CN	f (	126 - 136	) EQLsTsEENSK
53	α S2-CN	f (	126 - 137	) EQLSTsEENSKK
54	α S2-CN	f (	126 - 137	) EQLsTsEENSKK
55	α S2-CN	f (	126 - 137	) EQLsTsEEEnSKK
56				
57	α S2-CN	f (	128 - 136	) LSTsEENSK
58	α S2-CN	f (		
59				
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α S2-CN	f (	128 - 136	) LsTsEENSK
α S2-CN	f (	128 - 137	) LSTsEENSKK
α S2-CN	f (	137 - 146	) KTVDMesTEV
α S2-CN	f (	137 - 146	) KTVDMesTEV
α S2-CN	f (	137 - 147	) KTVDMesTEVF
α S2-CN	f (	137 - 148	) KTVDMesTEVFT
α S2-CN	f (	138 - 144	) TVDMesT
α S2-CN	f (	138 - 144	) TVDMesT
α S2-CN	f (	138 - 145	) TVDMesTE
α S2-CN	f (	138 - 145	) TVDMesTE
α S2-CN	f (	138 - 146	) TVDMesTEV
α S2-CN	f (	138 - 146	) TVDMesTEV
α S2-CN	f (	138 - 147	) TVDMesTEVF
α S2-CN	f (	138 - 148	) TVDMesTEVFT
α S2-CN	f (	138 - 149	) TVDMesTEVFTK
α S2-CN	f (	138 - 150	) TVDMesTEVFTKK
α S2-CN	f (	139 - 146	) VDMesTEV
α S2-CN	f (	140 - 146	) DMesTEV
α S2-CN	f (	140 - 148	) DMesTEVFT
α S2-CN	f (	141 - 146	) MEsTEV
β -CN	f (	1 - 16	) RELEELNVPGEIVeSL
β -CN	f (	2 - 16	) ELEELNVPGEIVeSL
β -CN	f (	3 - 16	) LEELNVPGEIVeSL
β -CN	f (	4 - 16	) EELNVPGEIVeSL
β -CN	f (	6 - 16	) LNVPGEIVeSL
β -CN	f (	6 - 24	) LNVPGEIVeSLssSEESIT
β -CN	f (	7 - 16	) NVPGEIVeSL
β -CN	f (	9 - 16	) PGEIVeSL
β -CN	f (	10 - 16	) GEIVeSL
β -CN	f (	11 - 16	) EIVeSL
β -CN	f (	12 - 24	) IVEsLssSEESIT
β -CN	f (	12 - 25	) IVEsLssSEESITR
β -CN	f (	15 - 22	) SLsssEES
β -CN	f (	15 - 24	) SLsssEESIT
β -CN	f (	15 - 25	) SLsssEESITR
β -CN	f (	16 - 22	) LSssEES
β -CN	f (	16 - 22	) LsssEES
β -CN	f (	16 - 24	) LsssEESIT
β -CN	f (	16 - 25	) LsssEESITR
β -CN	f (	16 - 26	) LsssEESITRI
β -CN	f (	17 - 22	) sssEES
β -CN	f (	17 - 24	) SssEESIT
β -CN	f (	17 - 24	) sssEESIT
β -CN	f (	17 - 25	) sssEESITR

1				
2	β -CN	f (	18 - 24	) ssEESIT
3	β -CN	f (	30 - 37	) IEKFQsEE
4	β -CN	f (	30 - 38	) IEKFQsEEQ
5	β -CN	f (	30 - 39	) IEKFQsEEQQ
6	β -CN	f (	30 - 40	) IEKFQsEEQQQ
7	β -CN	f (	30 - 40	) IEKFqEEQQQ
8	β -CN	f (	30 - 41	) IEKFQsEEQQQT
9	β -CN	f (	30 - 42	) IEKFQsEEQQQTE
10	β -CN	f (	30 - 43	) IEKFQsEEQQQTED
11	β -CN	f (	30 - 44	) IEKFQsEEQQQTEDE
12	β -CN	f (	30 - 44	) IEKFqEEQQQTEDE
13	β -CN	f (	30 - 45	) IEKFQsEEQQQTEDEL
14	β -CN	f (	30 - 45	) IEKFqEEQQQTEDEL
15	β -CN	f (	30 - 46	) IEKFQsEEQQQTEDELQ
16	β -CN	f (	30 - 47	) IEKFQsEEQQQTEDELQD
17	β -CN	f (	30 - 48	) IEKFQsEEQQQTEDELQDK
18	β -CN	f (	30 - 51	) IEKFQsEEQQQTEDELQDKIHP
19	β -CN	f (	31 - 43	) EKfQsEEQQQTED
20	β -CN	f (	31 - 44	) EKfQsEEQQQTEDE
21	β -CN	f (	31 - 45	) EKfQsEEQQQTEDEL
22	β -CN	f (	32 - 39	) KFQsEEQQ
23	β -CN	f (	32 - 40	) KFQsEEQQQ
24	β -CN	f (	32 - 42	) KFQsEEQQQTE
25	β -CN	f (	32 - 43	) KFQsEEQQQTED
26	β -CN	f (	32 - 44	) KFQsEEQQQTEDE
27	β -CN	f (	32 - 45	) KFQsEEQQQTEDEL
28	β -CN	f (	32 - 48	) KFQsEEQQQTEDELQDK
29	β -CN	f (	33 - 38	) FQsEEQ
30	β -CN	f (	33 - 39	) FQsEEQQ
31	β -CN	f (	33 - 40	) FQsEEQQQ
32	β -CN	f (	33 - 40	) FQsEEqQQ
33	β -CN	f (	33 - 41	) FQsEEQQQT
34	β -CN	f (	33 - 42	) FQsEEQQQTE
35	β -CN	f (	33 - 42	) FQsEEQqQTE
36	β -CN	f (	33 - 43	) FQsEEQQQTED
37	β -CN	f (	33 - 43	) FQsEEQQqTED
38	β -CN	f (	33 - 44	) FQsEEQQQTEDE
39	β -CN	f (	33 - 44	) FQsEEQQQTEDE
40	β -CN	f (	33 - 44	) FQsEEQQqTEDE
41	β -CN	f (	33 - 45	) FQsEEQQQTEDEL
42	β -CN	f (	33 - 45	) FQsEEqQQTEDEL
43	β -CN	f (	33 - 45	) FQsEEQQqTEDEL
44	β -CN	f (	33 - 46	) FQsEEQQQTEDELQ
45	β -CN	f (	33 - 47	) FQsEEQQQTEDELQD
46	β -CN	f (	33 - 48	) FQsEEQQQTEDELQDK
47	β -CN	f (	33 - 48	) FQsEEqQQTEDELQDK
48	β -CN	f (	33 - 51	) FQsEEQQQTEDELQDKIHP
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β -CN	f (	33 - 52	) FQsEEQQQTEDELQDKIHPF
β -CN	f (	34 - 44	) QsEEQQQTEDE
β -CN	f (	34 - 45	) QsEEQQQTEDEL
β -CN	f (	34 - 48	) QsEEQQQTEDELQDK
β -CN	f (	35 - 46	) sEEQQQTEDELQ
β -CN	f (	35 - 48	) sEEQQQTEDELQDK
β -CN	f (	120 - 126	) TEsQSLT
κ -CN A	f (	125 - 136	) IASGEPTStPt
κ -CN	f (	146 - 161	) LEDsPEVIESPPEINT
κ -CN	f (	147 - 161	) EDsPEVIESPPEINT
κ -CN	f (	153 - 165	) IESPPEINTVqVt

l extract of digesta of **Trentingrana (TN)** at **19 months** of ripening [digestion according the **PePan** protocol] with **CaCl₂** at pH value of:

Modifications	MH+ [Da]	Delta Mass [PPM]
S7(Phospho)	1026.486	-0.73
S7(Phospho); S12(Phospho); S14(Phospho)	2247.835	0.39
S7(Phospho); S12(Phospho); S14(Phospho)	2449.910	-0.73
S7(Phospho); S12(Phospho); S14(Phospho)	2578.954	-0.18
S7(Phospho); S12(Phospho); S14(Phospho)	2693.982	0.07
S6(Phospho); S11(Phospho); S13(Phospho)	2449.913	0.46
S5(Phospho)	769.348	-1.12
N2(Deamidated); S5(Phospho)	1055.467	0.85
S5(Phospho); S10(Phospho)	1350.522	-0.55
S5(Phospho); S10(Phospho); S12(Phospho)	1747.606	-2.95
S5(Phospho); S10(Phospho); S12(Phospho)	1862.636	-1.18
S12(Phospho); T13(Phospho)	1910.730	-0.49
N2(Deamidated); S10(Phospho); S12(Phospho)	1911.712	-1.14
S5(Phospho); S10(Phospho); S12(Phospho)	1990.696	-0.24
S5(Phospho); S10(Phospho); S12(Phospho)	2061.734	0.00
S5(Phospho); S10(Phospho); S12(Phospho)	2192.773	-0.66
S5(Phospho); S10(Phospho); S12(Phospho)	2321.814	-1.51
S5(Phospho); S10(Phospho); S12(Phospho); M18(Oxidation)	2337.813	0.36
S5(Phospho); S10(Phospho); S12(Phospho)	2436.844	0.12
S5(Phospho); S10(Phospho); S12(Phospho)	2678.027	1.36
S5(Phospho); S10(Phospho); S12(Phospho)	2937.123	0.17
S4(Phospho); S9(Phospho); S11(Phospho)	1891.627	-0.87
S8(Phospho); S10(Phospho)	1697.618	-0.69
S3(Phospho); S8(Phospho); S10(Phospho)	1777.585	-0.19
S7(Phospho); S9(Phospho)	1325.491	0.01
S7(Phospho); S9(Phospho)	1440.518	0.11
T10(Phospho)	1488.610	-0.20
S7(Phospho); S9(Phospho)	1568.577	0.03
S7(Phospho); S9(Phospho); Q13(Deamidated)	1569.562	1.20
S7(Phospho); S9(Phospho)	1639.613	-0.35
S2(Phospho); S7(Phospho); S9(Phospho)	1648.542	-0.43
S7(Phospho); S9(Phospho)	1770.655	0.31
S7(Phospho); S9(Phospho); Q13(Deamidated)	1771.638	-0.17
S7(Phospho); S9(Phospho)	1899.695	-0.80
S9(Phospho); T10(Phospho); Q13(Deamidated)	1900.681	0.29
S7(Phospho); S9(Phospho); M15(Oxidation)	1915.692	0.14
S7(Phospho); S9(Phospho)	2014.724	-0.07

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2	S7(Phospho); S9(Phospho); Q13(Deamidated)	2015.715	3.62
3	S7(Phospho); S9(Phospho); M15(Oxidation)	2030.719	0.39
4	S7(Phospho); S9(Phospho)	2127.808	-0.05
5	S7(Phospho); S9(Phospho)	2255.903	-0.05
6	S7(Phospho); S9(Phospho)	2383.961	-0.35
7	S7(Phospho); S9(Phospho)	2515.002	-0.03
8	S7(Phospho); S9(Phospho)	2644.046	0.58
9	S6(Phospho)	1375.525	-0.68
10	S6(Phospho); S8(Phospho)	1455.491	-0.83
11	S6(Phospho); S8(Phospho)	1526.529	-0.32
12	S1(Phospho); S6(Phospho); S8(Phospho)	1535.458	-0.56
13	S6(Phospho); S8(Phospho)	1657.569	-0.79
14	S8(Phospho); T9(Phospho)	1786.612	-0.66
15	S6(Phospho); S8(Phospho)	1901.639	-0.22
16	S6(Phospho); S8(Phospho)	2142.817	-0.69
17	S6(Phospho); S8(Phospho)	2270.874	-1.40
18	S6(Phospho); S8(Phospho)	2401.918	0.01
19	S8(Phospho); T9(Phospho)	2530.960	-0.14
20	S8(Phospho); T9(Phospho)	2731.042	0.63
21	S5(Phospho); S7(Phospho)	1368.459	-0.93
22	S5(Phospho); S7(Phospho)	1439.497	-0.13
23	S5(Phospho); S7(Phospho)	1570.537	-0.42
24	S5(Phospho); S7(Phospho)	1814.608	-0.01
25	S6(Phospho); T7(Phospho)	997.279	-1.43
26	S4(Phospho); S6(Phospho)	1112.307	-0.11
27	S4(Phospho)	1160.399	-0.03
28	S4(Phospho); S6(Phospho)	1240.365	-0.44
29	S4(Phospho)	1231.437	0.66
30	S4(Phospho); S6(Phospho)	1311.402	-0.28
31	S4(Phospho); S6(Phospho)	1442.443	-0.11
32	S4(Phospho); S6(Phospho)	1571.485	-0.34
33	S4(Phospho); S6(Phospho); M12(Oxidation)	1587.481	-0.05
34	S4(Phospho); S6(Phospho)	1686.511	-0.88
35	S4(Phospho); S6(Phospho)	1799.595	-0.94
36	S4(Phospho)	1847.725	-0.37
37	S4(Phospho); S6(Phospho)	1927.691	-0.37
38	S4(Phospho); S6(Phospho); M12(Oxidation)	1943.686	-0.07
39	S4(Phospho); S6(Phospho)	2055.749	-0.46
40	S4(Phospho); S6(Phospho); M12(Oxidation)	2071.745	-0.24
41	S4(Phospho); S6(Phospho)	2186.790	-0.53
42	S4(Phospho); S6(Phospho); M12(Oxidation)	2202.785	-0.32
43	S4(Phospho); S6(Phospho)	2315.832	-0.66
44	S4(Phospho); S6(Phospho)	2515.913	-0.17
45	S3(Phospho); S5(Phospho)	1125.338	-0.66
46	S3(Phospho); S5(Phospho)	1812.664	-0.34
47	S2(Phospho); S4(Phospho)	1012.253	-1.13
48	S8(Phospho)	1128.501	-0.05
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2	S6(Phospho)	887.322	0.60
3	S5(Phospho)	759.263	-0.36
4	S1(Phospho); S3(Phospho); S4(Phospho)	1401.463	0.69
5	S2(Phospho); S3(Phospho)	1234.465	0.74
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7	S2(Phospho); S3(Phospho); S4(Phospho)	1314.430	0.06
8	S2(Phospho); S3(Phospho); S10(Phospho)	1772.643	-0.16
9	S1(Phospho)	954.381	-0.22
10			
11	S1(Phospho); S2(Phospho)	1034.348	-0.17
12	S2(Phospho); S9(Phospho)	1605.646	0.62
13	S1(Phospho); S2(Phospho); S9(Phospho)	1685.611	-0.07
14	S7(Phospho)	1351.615	0.74
15	S3(Phospho)	881.376	-0.49
16	S6(Phospho)	1222.571	-0.38
17	S12(Phospho)	1537.767	0.42
18	S12(Phospho)	1795.850	-1.06
19	S12(Phospho)	1951.954	0.75
20			
21	N11(Deamidated); S12(Phospho)	1952.939	1.12
22	S11(Phospho)	1374.703	0.00
23	S11(Phospho)	1632.788	-0.37
24	S11(Phospho)	1788.888	-0.50
25			
26	N10(Deamidated); S11(Phospho)	1789.872	-0.50
27	S10(Phospho)	1660.795	0.35
28			
29	N9(Deamidated); S10(Phospho)	1661.780	0.86
30	S7(Phospho)	922.428	-0.02
31	S7(Phospho)	1180.515	1.42
32	S7(Phospho)	1336.614	-0.24
33	N6(Deamidated); S7(Phospho)	1337.598	-0.34
34	S6(Phospho)	809.343	-1.05
35	N5(Deamidated); S6(Phospho)	810.328	-0.38
36	S6(Phospho)	938.386	-0.97
37	S6(Phospho)	1067.429	-0.18
38	N5(Deamidated); S6(Phospho)	1068.413	-0.18
39	S6(Phospho)	1223.529	-0.79
40	N5(Deamidated); S6(Phospho)	1224.513	-1.09
41	S6(Phospho)	1336.615	0.22
42	S6(Phospho)	1473.673	-0.43
43	N5(Deamidated); S6(Phospho)	1474.660	1.88
44	S5(Phospho)	1094.487	-0.33
45	N4(Deamidated); S5(Phospho)	1095.471	-0.56
46	S4(Phospho)	981.403	-1.13
47	N3(Deamidated); S4(Phospho)	982.386	-1.39
48	S3(Phospho)	726.234	-0.80
49	N2(Deamidated); S3(Phospho)	727.218	-0.64
50	S3(Phospho)	882.334	-1.05
51	N2(Deamidated); S3(Phospho)	1133.460	-1.84
52	S2(Phospho)	1345.567	-3.78
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2	S6(Phospho)	880.312	-0.10
3	S5(Phospho)	717.249	-0.51
4	S9(Phospho)	1566.669	0.31
5	T16(Phospho)	2109.941	0.06
6			
7	S8(Phospho); S9(Phospho); S10(Phospho)	1617.493	-0.57
8	S10(Phospho); S13(Phospho); S16(Phospho)	2375.876	0.14
9			
10	S2(Phospho); S3(Phospho); S4(Phospho)	964.198	-0.41
11	S1(Phospho); S2(Phospho); S3(Phospho)	865.130	-0.53
12	S1(Phospho); S2(Phospho)	924.300	0.13
13	S1(Phospho); S2(Phospho)	1011.333	0.67
14	S1(Phospho); S2(Phospho); S5(Phospho)	1348.400	0.44
15			
16	S4(Phospho)	756.317	-0.30
17	S4(Phospho)	857.365	-0.85
18	S3(Phospho)	770.333	0.14
19	S9(Phospho)	1567.719	0.09
20	S7(Phospho)	1197.497	-0.33
21	S7(Phospho)	1310.581	0.01
22			
23	N1(Deamidated); S7(Phospho)	1311.565	-0.46
24	M2(Oxidation); S7(Phospho)	1326.576	-0.02
25			
26	S6(Phospho)	1083.455	0.50
27	S6(Phospho)	1196.538	-0.13
28	S5(Phospho)	1065.498	0.63
29	N3(Deamidated); S5(Phospho)	1066.482	0.51
30	S3(Phospho)	881.376	-0.01
31	S2(Phospho)	767.333	-0.14
32			
33	S4(Phospho); S5(Phospho); S6(Phospho)	2078.750	0.26
34	S1(Phospho)	1014.403	0.49
35	T3(Phospho)	727.291	-0.16
36			
37	S3(Phospho); S5(Phospho)	1282.460	-0.11
38	S4(Phospho)	890.284	-1.21
39			
40	S6(Phospho); S8(Phospho)	1352.477	0.17
41	S6(Phospho); S8(Phospho)	1466.519	-0.56
42	S6(Phospho); S8(Phospho)	1553.551	-0.41
43	S8(Phospho)	1601.679	-0.68
44	S6(Phospho); S8(Phospho)	1681.646	-0.66
45	S6(Phospho); S8(Phospho); N11(Deamidated)	1682.629	-0.74
46	S6(Phospho); S8(Phospho)	1809.740	-1.16
47			
48	S6(Phospho); S8(Phospho); N11(Deamidated)	1810.725	-0.22
49	S6(Phospho); S8(Phospho); S12(Phospho)	1889.707	-0.41
50	S5(Phospho); S7(Phospho)	1695.698	-0.61
51			
52	S4(Phospho)	1331.536	-0.08
53	S4(Phospho); S6(Phospho)	1411.502	-0.79
54	S6(Phospho)	1459.630	-0.91
55	S4(Phospho); S6(Phospho)	1539.597	-0.56
56	S4(Phospho); S6(Phospho); N9(Deamidated)	1540.580	-0.88
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58	S4(Phospho)	1074.436	0.90
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2	S2(Phospho); S4(Phospho)	1154.401	-0.55
3	S4(Phospho)	1202.529	-0.92
4	S7(Phospho)	1218.496	0.00
5			
6	M5(Oxidation); T8(Phospho)	1234.491	0.26
7	S7(Phospho)	1365.563	-0.85
8	S7(Phospho)	1466.612	-0.43
9			
10	S6(Phospho)	862.290	-0.20
11	T7(Phospho)	862.290	-0.06
12	T7(Phospho)	991.332	-0.61
13	S6(Phospho)	991.334	0.99
14	T7(Phospho)	1090.401	-0.23
15			
16	M4(Oxidation); T7(Phospho)	1106.396	
17	M4(Oxidation); S6(Phospho)	1106.396	
18	S6(Phospho)	1237.470	0.30
19	T7(Phospho)	1338.518	0.26
20			
21	S6(Phospho)	1466.612	-0.26
22	S6(Phospho)	1594.707	-0.24
23	S5(Phospho)	989.353	-0.16
24	S4(Phospho)	890.285	-0.25
25	S4(Phospho)	1138.401	-0.05
26			
27	S3(Phospho)	775.258	-0.40
28	S15(Phospho)	1905.921	0.05
29	S14(Phospho)	1749.820	0.22
30			
31	S13(Phospho)	1620.777	-0.14
32	S12(Phospho)	1507.692	-0.50
33	S10(Phospho)	1249.608	0.46
34	S10(Phospho); S12(Phospho); S13(Phospho)	2229.884	-0.46
35			
36	S9(Phospho)	1136.523	-0.49
37	S7(Phospho)	923.412	-0.30
38	S6(Phospho)	826.359	-0.07
39	S5(Phospho)	769.338	-0.17
40			
41	S4(Phospho); S6(Phospho); S7(Phospho)	1620.573	0.20
42	S4(Phospho); S6(Phospho); S7(Phospho)	1776.674	0.08
43	S3(Phospho); S4(Phospho); S5(Phospho)	1065.249	2.83
44	S3(Phospho); S4(Phospho); S5(Phospho)	1279.378	0.32
45			
46	S3(Phospho); S4(Phospho); S5(Phospho)	1435.479	-0.31
47	S3(Phospho); S4(Phospho)	898.247	-0.85
48			
49	S2(Phospho); S3(Phospho); S4(Phospho)	978.215	0.57
50	S2(Phospho); S3(Phospho); S4(Phospho)	1192.346	-0.09
51			
52	S2(Phospho); S3(Phospho); S4(Phospho)	1348.447	0.13
53	S2(Phospho); S3(Phospho); S4(Phospho)	1461.531	0.01
54	S1(Phospho); S2(Phospho); S3(Phospho)	865.130	-0.53
55	S2(Phospho); S3(Phospho)	999.295	-0.59
56			
57	S1(Phospho); S2(Phospho); S3(Phospho)	1079.262	-0.29
58	S1(Phospho); S2(Phospho); S3(Phospho)	1235.363	0.25
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2	S1(Phospho); S2(Phospho)	912.263	-0.46
3	S6(Phospho)	1089.450	-0.04
4	S6(Phospho)	1217.508	-0.73
5	S6(Phospho)	1345.567	-0.28
6	S6(Phospho)	1473.625	-0.83
7	Q5(Deamidated); S6(Phospho)	1474.611	0.49
8	S6(Phospho)	1574.673	-0.51
9	S6(Phospho)	1703.715	-0.76
10	S6(Phospho)	1818.741	-1.10
11	S6(Phospho)	1947.784	-0.77
12	Q5(Deamidated); S6(Phospho)	1948.770	0.04
13	S6(Phospho)	2060.870	0.23
14	Q5(Deamidated); S6(Phospho)	2061.854	0.05
15	S6(Phospho)	2188.928	-0.11
16	S6(Phospho)	2303.952	-1.52
17	S6(Phospho)	2432.048	-0.84
18	S6(Phospho)	2779.245	-0.28
19	S5(Phospho)	1705.659	0.02
20	S5(Phospho)	1834.702	0.02
21	S5(Phospho)	1947.784	-0.77
22	S4(Phospho)	1103.440	-0.27
23	S4(Phospho)	1231.498	-0.73
24	S4(Phospho)	1461.589	-0.49
25	S4(Phospho)	1576.617	0.26
26	S4(Phospho)	1705.659	0.02
27	S4(Phospho)	1818.741	-1.37
28	S4(Phospho)	2189.924	0.39
29	S3(Phospho)	847.287	0.15
30	S3(Phospho)	975.344	-1.80
31	S3(Phospho)	1103.403	-0.92
32	S3(Phospho); Q6(Deamidated)	1104.388	-0.38
33	S3(Phospho)	1204.451	-0.40
34	S3(Phospho)	1333.493	-1.09
35	S3(Phospho); Q7(Deamidated)	1334.478	-0.18
36	S3(Phospho)	1448.521	-0.48
37	S3(Phospho); Q8(Deamidated)	1449.506	0.36
38	S3(Phospho)	1577.563	-0.75
39	Q2(Deamidated); S3(Phospho)	1578.547	-0.52
40	S3(Phospho); Q8(Deamidated)	1578.549	0.41
41	S3(Phospho)	1690.647	-0.46
42	S3(Phospho); Q6(Deamidated)	1691.633	0.40
43	S3(Phospho); Q8(Deamidated)	1691.636	2.49
44	S3(Phospho)	1818.705	-0.82
45	S3(Phospho)	1933.733	-0.07
46	S3(Phospho)	2061.830	0.65
47	S3(Phospho); Q6(Deamidated)	2062.812	-0.12
48	S3(Phospho)	2409.021	-1.25
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2	S3(Phospho)	2556.090	-1.10
3	S2(Phospho)	1430.495	-0.19
4	S2(Phospho)	1543.579	-0.54
5	S2(Phospho)	1914.759	-0.42
6	S1(Phospho)	1543.579	-0.54
7	S1(Phospho)	1786.700	-0.73
8	S3(Phospho)	845.329	0.60
9			
10	T9(Phospho); T11(Phospho); T12(Phospho)	1401.462	-0.53
11	S4(Phospho)	1848.815	0.05
12	S3(Phospho)	1735.732	0.32
13	Q11(Deamidated); T13(Phospho)	1507.692	-0.33
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For Peer Review

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RT [min]	Color code	Number of phosphorylated serine residues per peptide	Number of phosphorylated threonine residues per peptide
4.8	b	1	0
8.4	r	3	0
9.9	r	3	0
9.7	r	3	0
10.2	r	3	0
9.4	r	3	0
4.1	b	1	0
9.5	n	1	0
8.9	r	2	0
8.5	r	3	0
8.5	r	3	0
8.4	r	1	1
8.6	r	2	0
8.7	r	3	0
8.8	r	3	0
10.4	r	3	0
9.8	r	3	0
8.8	r	3	0
10.4	r	3	0
11.3	r	3	0
15.2	r	3	0
7.7	r	3	0
7.0	r	2	0
7.1	r	3	0
6.4	r	2	0
6.4	r	2	0
6.3	b	0	1
6.2	b	2	0
6.7	r	2	0
7.1	r	2	0
5.8	r	3	0
8.4	r	2	0
9.3	r	2	0
8.2	r	2	0
9.1	r	1	1
7.1	r	2	0
8.1	r	2	0

1		2	0
2	9.1 r	2	0
3	7.2 r	2	0
4	12.8 r	2	0
5	11.5 r	2	0
6	11.4 r	2	0
7	14.6 r	2	0
8	14.9 r	2	0
9	4.0 n	1	0
10	3.5 b	2	0
11	5.3 r	2	0
12	2.9 r	3	0
13	7.7 r	2	0
14	7.0 r	1	1
15	6.8 r	2	0
16	10.9 r	2	0
17	10.8 r	2	0
18	12.6 r	2	0
19	14.5 r	1	1
20	15.2 r	1	1
21	3.5 r	2	0
22	5.3 r	2	0
23	7.1 r	2	0
24	7.0 r	2	0
25	3.6 r	1	1
26	4.0 r	2	0
27	5.0 b	1	0
28	5.0 b	2	0
29	6.2 n	1	0
30	5.6 r	2	0
31	7.4 r	2	0
32	7.4 r	2	0
33	6.0 r	2	0
34	7.7 r	2	0
35	13.0 r	2	0
36	11.5 n	1	0
37	11.5 b	2	0
38	9.0 r	2	0
39	9.8 r	2	0
40	9.0 r	2	0
41	13.3 r	2	0
42	12.4 r	2	0
43	15.3 r	2	0
44	16.0 r	2	0
45	2.8 r	2	0
46	11.2 r	2	0
47	4.5 r	2	0
48	9.7 r	1	0
49			
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2	8.6 b	1	0
3	8.5 n	1	0
4	10.4 r	3	0
5	9.5 r	2	0
6	9.7 r	3	0
7	8.8 r	3	0
8	8.5 n	1	0
9	8.0 r	2	0
10	9.0 b	2	0
11	8.7 r	3	0
12	9.0 n	1	0
13	8.9 b	1	0
14	8.5 n	1	0
15	15.2 n	1	0
16	15.1 n	1	0
17	14.3 b	1	0
18	14.7 n	1	0
19	14.0 n	1	0
20	13.8 n	1	0
21	13.0 b	1	0
22	13.4 n	1	0
23	13.5 b	1	0
24	13.8 n	1	0
25	11.8 b	1	0
26	11.6 b	1	0
27	11.2 b	1	0
28	11.4 b	1	0
29	8.0 b	1	0
30	8.7 b	1	0
31	7.8 n	1	0
32	8.1 b	1	0
33	8.7 b	1	0
34	7.7 b	1	0
35	8.2 b	1	0
36	11.9 b	1	0
37	9.9 r	1	0
38	9.9 n	1	0
39	5.8 b	1	0
40	6.1 n	1	0
41	7.6 b	1	0
42	8.1 b	1	0
43	8.1 b	1	0
44	8.7 n	1	0
45	7.5 b	1	0
46	9.9 b	1	0
47	6.8 b	1	0
48			
49			
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1			
2	10.5 n	1	0
3	9.3 b	1	0
4	10.9 n	1	0
5	15.5 n	0	1
6			
7	5.3 r	3	0
8	11.2 r	3	0
9			
10	2.4 r	3	0
11	2.7 r	3	0
12	10.6 r	2	0
13	9.5 r	2	0
14	9.6 r	3	0
15			
16	9.4 b	1	0
17	10.0 n	1	0
18	7.1 n	1	0
19			
20	10.4 n	1	0
21	7.4 n	1	0
22	11.4 n	1	0
23	11.6 n	1	0
24			
25	9.4 n	1	0
26	7.0 n	1	0
27	11.2 n	1	0
28	8.9 n	1	0
29			
30	9.8 n	1	0
31	8.9 n	1	0
32	9.0 n	1	0
33			
34	9.5 r	3	0
35	8.6 n	1	0
36	6.5 n	0	1
37	2.8 r	2	0
38			
39	9.2 n	1	0
40	5.1 r	2	0
41	4.3 r	2	0
42	4.5 b	2	0
43	4.7 r	1	0
44			
45	4.3 b	2	0
46	3.9 r	2	0
47	3.5 b	2	0
48	3.3 r	2	0
49	3.0 r	3	0
50	3.4 r	2	0
51			
52	4.5 n	1	0
53	3.8 b	2	0
54			
55	3.7 n	1	0
56	3.3 b	2	0
57	3.1 r	2	0
58			
59	2.7 n	1	0
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2	2.5 r	2	0
3	2.2 n	1	0
4	9.4 b	1	0
5	6.2 n	0	1
6	13.2 r	1	0
7	12.3 b	1	0
8	6.1 n	1	0
9	6.1 r	0	1
10	6.3 r	0	1
11	6.3 n	1	0
12	9.6 b	0	1
13	r	0	1
14	n	1	0
15	13.7 b	1	0
16	12.8 b	0	1
17	12.0 r	1	0
18	11.2 r	1	0
19	9.4 n	1	0
20	9.2 r	1	0
21	11.8 r	1	0
22	6.5 b	1	0
23	17.3 b	1	0
24	17.9 r	1	0
25	17.6 b	1	0
26	16.4 b	1	0
27	16.1 b	1	0
28	18.2 r	3	0
29	14.1 b	1	0
30	16.1 b	1	0
31	12.2 r	1	0
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34	10.3 r	3	0
35	3.2 r	3	0
36	8.7 r	3	0
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38	1.9 r	2	0
39	1.9 r	3	0
40	7.3 r	3	0
41	6.9 r	3	0
42	12.0 r	3	0
43	2.7 r	3	0
44	5.1 r	2	0
45	5.7 r	3	0
46	4.8 r	3	0
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5	6.8 b	1	0
6	6.9 b	1	0
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13	10.5 b	1	0
14	11.4 b	1	0
15	9.4 b	1	0
16	10.2 b	1	0
17	9.9 b	1	0
18	11.1 n	1	0
19	6.0 n	1	0
20	6.7 r	1	0
21	10.2 n	1	0
22	3.6 n	1	0
23	3.8 n	1	0
24	5.3 n	1	0
25	5.4 b	1	0
26	6.0 b	1	0
27	10.0 n	1	0
28	9.0 n	1	0
29	2.9 b	1	0
30	3.1 b	1	0
31	3.0 b	1	0
32	3.8 n	1	0
33	4.3 n	1	0
34	4.7 b	1	0
35	5.2 n	1	0
36	5.0 b	1	0
37	5.4 r	1	0
38	5.6 b	1	0
39	6.4 r	1	0
40	6.2 n	1	0
41	10.4 b	1	0
42	10.5 n	1	0
43	10.5 r	1	0
44	7.9 b	1	0
45	8.1 r	1	0
46	8.5 b	1	0
47	9.8 b	1	0
48	10.8 b	1	0
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2	14.8 b	1	0
3	2.1 b	1	0
4	8.3 b	1	0
5	7.3 b	1	0
6	8.3 b	1	0
7	7.2 b	1	0
8	5.1 n	1	0
9			
10	10.3 r	0	3
11	13.2 n	1	0
12	12.8 b	1	0
13	16.5 b	0	1
14			
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Number of phosphorylated residues per peptides	Peptide length	Max peptide length	Min peptide length
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3	18		
3	20		
3	21		
3	22		
3	20		
1	6		
1	9		
2	11		
3	14		
3	15		
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2	16		
2	16		
2	16		
2	17		

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5	2	19
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7	2	21
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27	2	8
28	2	9
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30	2	10
31	2	11
32	2	11
33	1	12
34	2	13
35		
36	1	14
37	2	15
38	2	16
39	2	17
40	2	17
41	2	18
42	2	18
43	2	19
44	1	21
45	2	9
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51	2	
52	2	
53	2	
54	2	
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56	2	
57	2	
58	2	
59	1	
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7	3	14
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11	3	13
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54	2	8
55	3	8
56	3	9
57	3	
58	3	
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10	3	16
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Supplementary Table S1. TN_26. Caseinophosphopeptides identified in enriched extra CPPs isolated from cheese digesta by selective precipitation with pH 8.0 are indicated in black; pH 4.6 are indicated in red; both, pH 8.0 and pH 4.6, are indicated in blue.

Protein fragment			Sequence
α S1-CN	f (	35 - 42	) EKVNELsK
α S1-CN	f (	35 - 50	) EKVNELsKDIGsEsTE
α S1-CN	f (	35 - 52	) EKVNELsKDIGsEsTEDQ
α S1-CN	f (	35 - 53	) EKVNELsKDIGsEsTEDQA
α S1-CN	f (	35 - 54	) EKVNELsKDIGsEsTEDQAM
α S1-CN	f (	35 - 55	) EKVNELsKDIGsEsTEDQAME
α S1-CN	f (	35 - 56	) EKVNELsKDIGsEsTEDQAMED
α S1-CN	f (	36 - 42	) KVNELsK
α S1-CN	f (	36 - 52	) KVNELsKDIGsEsTEDQ
α S1-CN	f (	36 - 53	) KVNELsKDIGsEsTEDQA
α S1-CN	f (	36 - 55	) KVNELsKDIGsEsTEDQAME
α S1-CN	f (	36 - 56	) KVNELsKDIGsEsTEDQAMED
α S1-CN	f (	37 - 42	) VNELsK
α S1-CN	f (	37 - 45	) VNELsKDIG
α S1-CN	f (	37 - 45	) VnELsKDIG
α S1-CN	f (	37 - 47	) VNELsKDIGsE
α S1-CN	f (	37 - 50	) VNELsKDIGsEsTE
α S1-CN	f (	37 - 52	) VNELsKDIGsESTEDQ
α S1-CN	f (	37 - 52	) VnELsKDIGsEsTEDQ
α S1-CN	f (	37 - 52	) VNELsKDIGsEsTEDQ
α S1-CN	f (	37 - 53	) VNELsKDIGsEsTEDQA
α S1-CN	f (	37 - 54	) VNELsKDIGsEsTEDQAM
α S1-CN	f (	37 - 55	) VNELsKDIGsEsTEDQAME
α S1-CN	f (	37 - 56	) VNELsKDIGsEsTEDQAMED
α S1-CN	f (	37 - 60	) VNELsKDIGsEsTEDQAMEDIKQM
α S1-CN	f (	38 - 52	) NELsKDIGsEsTEDQ
α S1-CN	f (	39 - 52	) ELsKDIGsEsTEDQ
α S1-CN	f (	39 - 52	) ELsKDIGsEsTEDQ
α S1-CN	f (	40 - 50	) LSKDIGsEsTE
α S1-CN	f (	40 - 51	) LSKDIGsEsTED
α S1-CN	f (	40 - 52	) LSKDIGsEsTEDQ
α S1-CN	f (	40 - 52	) LSKDIGsEsTEDQ
α S1-CN	f (	40 - 52	) LSKDIGsEsTEDq
α S1-CN	f (	40 - 53	) LSKDIGsEsTEDQA
α S1-CN	f (	40 - 53	) LSKDIGsEsTEDqA
α S1-CN	f (	40 - 52	) LsKDIGsEsTEDQ
α S1-CN	f (	40 - 54	) LSKDIGsEsTEDQAM

1				
2	α S1-CN	f (	40 - 54	) LSKDIGsEsTEDqAM
3	α S1-CN	f (	40 - 55	) LSKDIGsEsTEDQAME
4	α S1-CN	f (	40 - 55	) LSKDIGSEstEDqAME
5	α S1-CN	f (	40 - 55	) LSKDIGsEsTEDQAmE
6	α S1-CN	f (	40 - 56	) LSKDIGsEsTEDQAMED
7	α S1-CN	f (	40 - 56	) LSKDIGsEsTEDqAMED
8	α S1-CN	f (	40 - 56	) LSKDIGsEsTEDQAmED
9	α S1-CN	f (	40 - 58	) LSKDIGsEsTEDQAMEDIK
10	α S1-CN	f (	40 - 59	) LSKDIGSEstEDQAMEDIKQ
11	α S1-CN	f (	40 - 60	) LSKDIGsEsTEDQAMEDIKQM
12	α S1-CN	f (	41 - 50	) SKDIGsEsTE
13	α S1-CN	f (	41 - 52	) SKDIGsEsTEDQ
14	α S1-CN	f (	41 - 52	) SKDIGsEsTEDq
15	α S1-CN	f (	41 - 53	) SKDIGsEsTEDQA
16	α S1-CN	f (	41 - 52	) sKDIGsEsTEDQ
17	α S1-CN	f (	41 - 54	) SKDIGsEsTEDQAM
18	α S1-CN	f (	41 - 55	) SKDIGsEsTEDQAME
19	α S1-CN	f (	41 - 55	) SKDIGsEsTEDQAmE
20	α S1-CN	f (	41 - 56	) SKDIGsEsTEDQAMED
21	α S1-CN	f (	41 - 58	) SKDIGsEsTEDQAMEDIK
22	α S1-CN	f (	41 - 59	) SKDIGsEsTEDQAMEDIKQ
23	α S1-CN	f (	41 - 60	) SKDIGsEsTEDQAMEDIKQM
24	α S1-CN	f (	42 - 50	) KDIGsEsTE
25	α S1-CN	f (	42 - 52	) KDIGsEsTEDQ
26	α S1-CN	f (	42 - 53	) KDIGsEsTEDQA
27	α S1-CN	f (	42 - 54	) KDIGsEsTEDQAM
28	α S1-CN	f (	42 - 56	) KDIGsEsTEDQAMED
29	α S1-CN	f (	43 - 50	) DIGsEsTE
30	α S1-CN	f (	43 - 51	) DIGsEsTED
31	α S1-CN	f (	43 - 52	) DIGsESTEDQ
32	α S1-CN	f (	43 - 52	) DIGsEsTEDQ
33	α S1-CN	f (	43 - 53	) DIGsEsTEDQA
34	α S1-CN	f (	43 - 54	) DIGsEsTEDQAM
35	α S1-CN	f (	43 - 55	) DIGsEsTEDQAME
36	α S1-CN	f (	43 - 55	) DIGsEsTEDQAmE
37	α S1-CN	f (	43 - 56	) DIGsEsTEDQAMED
38	α S1-CN	f (	43 - 58	) DIGsEsTEDQAMEDIK
39	α S1-CN	f (	43 - 58	) DIGsEsTEDqAMEDIK
40	α S1-CN	f (	43 - 58	) DIGsEsTEDQAmEDIK
41	α S1-CN	f (	43 - 59	) DIGsEsTEDQAMEDIKQ
42	α S1-CN	f (	43 - 59	) DIGsEsTEDQAmEDIKQ
43	α S1-CN	f (	43 - 60	) DIGsEsTEDQAMEDIKQM
44	α S1-CN	f (	43 - 60	) DIGsEsTEDQAmEDIKQM
45	α S1-CN	f (	43 - 61	) DIGsEsTEDQAMEDIKQME
46	α S1-CN	f (	43 - 63	) DIGsEsTEDQAMEDIKQMEAE
47	α S1-CN	f (	44 - 52	) IGsEsTEDQ
48	α S1-CN	f (	45 - 52	) GsEsTEDQ
49				
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2	α S1-CN	f (	46 - 54	) sEsTEDQAM
3	α S1-CN	f (	57 - 65	) IKQMEAEsI
4	α S1-CN	f (	59 - 65	) QMEAEsI
5				
6	α S1-CN	f (	64 - 74	) SIssEEIVPN
7	α S1-CN	f (	65 - 74	) IssSEEIVPN
8	α S1-CN	f (	65 - 74	) IssEEIVPN
9				
10	α S1-CN	f (	65 - 79	) ISssEEIVPNsVEQK
11	α S1-CN	f (	66 - 79	) SssEEIVPNsVEQK
12	α S1-CN	f (	67 - 74	) sSEEIVPN
13	α S1-CN	f (	67 - 74	) ssEEIVPN
14	α S1-CN	f (	67 - 74	) ssEEIVPn
15	α S1-CN	f (	67 - 79	) SsEEIVPNsVEQK
16	α S1-CN	f (	67 - 79	) ssEEIVPNsVEQK
17	α S1-CN	f (	69 - 78	) IVPNsVEQK
18				
19	α S1-CN	f (	69 - 78	) IVPnsVEQK
20	α S1-CN	f (	69 - 78	) EIVPNsVEQK
21	α S1-CN	f (	69 - 78	) EIVPnsVEQK
22	α S1-CN	f (	69 - 79	) EEIVPNsVEQK
23	α S1-CN	f (	73 - 79	) PNsVEQK
24				
25	α S1-CN	f (	104 - 116	) YKVPQLEIVPNsA
26	α S1-CN	f (	104 - 118	) YKVPQLEIVPNsAEE
27	α S1-CN	f (	104 - 119	) YKVPQLEIVPNsAEER
28	α S1-CN	f (	105 - 116	) KVPQLEIVPNsA
29	α S1-CN	f (	105 - 118	) KVPQLEIVPNsAEE
30	α S1-CN	f (	105 - 119	) KVPQLEIVPNsAEER
31	α S1-CN	f (	106 - 119	) VPQLEIVPNsAEER
32	α S1-CN	f (	106 - 119	) VPQLEIVPnsAEER
33	α S1-CN	f (	108 - 119	) QLEIVPNsAEER
34	α S1-CN	f (	109 - 116	) LEIVPNsA
35	α S1-CN	f (	109 - 118	) LEIVPNsAEE
36	α S1-CN	f (	109 - 119	) LEIVPNsAEER
37	α S1-CN	f (	109 - 119	) LEIVPnsAEER
38	α S1-CN	f (	109 - 120	) LEIVPNsAEERL
39	α S1-CN	f (	110 - 116	) EIVPNsA
40	α S1-CN	f (	110 - 116	) EIVPnsA
41	α S1-CN	f (	110 - 117	) EIVPNsAE
42	α S1-CN	f (	110 - 117	) EIVPnsAE
43	α S1-CN	f (	110 - 118	) EIVPNsAEE
44	α S1-CN	f (	110 - 118	) EIVPnsAEE
45	α S1-CN	f (	110 - 119	) EIVPNsAEER
46	α S1-CN	f (	110 - 119	) EIVPnsAEER
47	α S1-CN	f (	110 - 120	) EIVPNsAEERL
48	α S1-CN	f (	110 - 121	) EIVPNsAEERLH
49	α S1-CN	f (	110 - 121	) EIVPnsAEERLH
50	α S1-CN	f (	110 - 123	) EIVPnsAEERLHSM
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2	α S1-CN	f (	111 - 119	) IVPNsAEER
3	α S1-CN	f (	111 - 119	) IVPNsAEER
4	α S1-CN	f (	112 - 119	) VPNsAEER
5	α S1-CN	f (	112 - 119	) VPnsAEER
6	α S1-CN	f (	113 - 118	) PNsAEE
7	α S1-CN	f (	113 - 119	) PNsAEER
8	α S1-CN	f (	113 - 121	) PnsAEERLH
9	α S1-CN	f (	114 - 119	) NsAEER
10	α S1-CN	f (	121 - 131	) HsMKEGIHAQQ
11	α S1-CN	f (	173 - 179	) YTDAPsF
12	α S1-CN	f (	173 - 186	) YTDAPsFSDIPNPI
13	α S1-CN	f (	174 - 179	) TDAPsF
14	α S1-CN	f (	180 - 193	) SDIPNPIGsENSEK
15	α S1-CN B	f (	180 - 194	) SDIPNPIGSENSsEKT
16	α S1-CN B	f (	180 - 198	) SDIPNPIGSENSEKtTMPL
17	α S2-CN	f (	1 - 12	) KNTMEHVsssEE
18	α S2-CN	f (	7 - 13	) VsssEES
19	α S2-CN	f (	8&56 - 13&61	) sssEES
20	α S2-CN	f (	9 - 14	) ssEESI
21	α S2-CN	f (	9 - 16	) ssEESIIS
22	α S2-CN	f (	13 - 18	) SIIsQE
23	α S2-CN	f (	13 - 19	) SIIsQET
24	α S2-CN	f (	14 - 19	) IIsQET
25	α S2-CN	f (	23 - 35	) EKNMAINPsKENL
26	α S2-CN	f (	25 - 134	) NMAINPsKEN
27	α S2-CN	f (	25 - 135	) NMAINPsKENL
28	α S2-CN	f (	25 - 135	) nMAINPsKENL
29	α S2-CN	f (	25 - 135	) NmAINPsKENL
30	α S2-CN	f (	26 - 34	) MAINPsKEN
31	α S2-CN	f (	26 - 35	) MAINPsKENL
32	α S2-CN	f (	27 - 35	) AINPsKENL
33	α S2-CN	f (	27 - 35	) AInPsKENL
34	α S2-CN	f (	29 - 35	) NPsKENL
35	α S2-CN	f (	30 - 35	) PsKENL
36	α S2-CN	f (	53 - 70	) SIGSssEEsAEVATEEVK
37	α S2-CN	f (	64 - 70	) VAtEEVK
38	α S2-CN	f (	124 - 133	) NREQLsTsEE
39	α S2-CN	f (	124 - 134	) NREQLsTsEEN
40	α S2-CN	f (	124 - 135	) NREQLsTsEENS
41	α S2-CN	f (	124 - 136	) NREQLSTsEENSK
42	α S2-CN	f (	124 - 136	) NREQLsTsEENSK
43	α S2-CN	f (	124 - 136	) NREQLsTsEEnSK
44	α S2-CN	f (	124 - 137	) NREQLsTsEENSKK
45	α S2-CN	f (	124 - 137	) NREQLsTsEEnSKK
46	α S2-CN	f (	124 - 137	) NREQLsTsEENsKK
47	α S2-CN	f (	124 - 138	) NREQLsTsEEnSKKT
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2	α S2-CN	f (	124 - 146	) NREQLsTsEENSsKKTVDMEStEV
3	α S2-CN	f (	125 - 137	) REQLsTsEENSsKK
4	α S2-CN	f (	126 - 136	) EQLSTsEENSsK
5	α S2-CN	f (	126 - 136	) EQLsTsEENSsK
6	α S2-CN	f (	126 - 137	) EQLSTsEENSsKK
7	α S2-CN	f (	126 - 137	) EQLsTsEENSsKK
8	α S2-CN	f (	128 - 136	) LSTsEENSsK
9	α S2-CN	f (	128 - 137	) LSTsEENSsKK
10	α S2-CN	f (	137 - 146	) KTVDMESStEV
11	α S2-CN	f (	137 - 146	) KTVDMESStEV
12	α S2-CN	f (	137 - 148	) KTVDMESStEVFT
13	α S2-CN	f (	137 - 148	) KTVDMESStEVFT
14	α S2-CN	f (	138 - 144	) TVDMESSt
15	α S2-CN	f (	138 - 145	) TVDMESStE
16	α S2-CN	f (	138 - 145	) TVDMESStE
17	α S2-CN	f (	138 - 146	) TVDMESStEV
18	α S2-CN	f (	138 - 146	) TVDMESStEV
19	α S2-CN	f (	138 - 147	) TVDMESStEVF
20	α S2-CN	f (	138 - 147	) TVDMESStEVF
21	α S2-CN	f (	138 - 148	) TVDMESStEVFT
22	α S2-CN	f (	138 - 149	) TVDMESStEVFTK
23	α S2-CN	f (	138 - 150	) TVDMESStEVFTKK
24	α S2-CN	f (	140 - 146	) DMESStEV
25	α S2-CN	f (	140 - 146	) DMESStEV
26	α S2-CN	f (	141 - 146	) MESStEV
27	β -CN	f (	1 - 16	) RELEELNVPGEIVESL
28	β -CN	f (	2 - 16	) ELEELNVPGEIVESL
29	β -CN	f (	3 - 16	) LEELNVPGEIVESL
30	β -CN	f (	4 - 16	) EELNVPGEIVESL
31	β -CN	f (	5 - 16	) ELNVPGEIVESL
32	β -CN	f (	6 - 16	) LNVPGEIVESL
33	β -CN	f (	6 - 24	) LNVPGEIVESLsssEESIT
34	β -CN	f (	7 - 16	) NVPGEIVESL
35	β -CN	f (	9 - 16	) PGEIVESL
36	β -CN	f (	11 - 16	) EIVESL
37	β -CN	f (	12 - 25	) IVESLsssEESITR
38	β -CN	f (	15 - 22	) SLsssEES
39	β -CN	f (	15 - 24	) SLsssEESIT
40	β -CN	f (	15 - 25	) SLsssEESITR
41	β -CN	f (	16 - 22	) LssSEES
42	β -CN	f (	16 - 22	) LsssEES
43	β -CN	f (	16 - 24	) LsssEESIT
44	β -CN	f (	16 - 25	) LsssEESITR

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2	β -CN	f (	16 - 26	) LsssEEsITRI
3	β -CN	f (	17 - 22	) sssEES
4	β -CN	f (	17 - 24	) ssSEESIT
5	β -CN	f (	17 - 24	) sssEESIT
6	β -CN	f (	17 - 25	) sssEESITR
7	β -CN	f (	18 - 23	) ssEESI
8	β -CN	f (	18 - 24	) ssEESIT
9	β -CN	f (	29 - 44	) KIEKFQsEEQQQTEDE
10	β -CN	f (	29 - 44	) KIEKFqsEEQQQTEDE
11	β -CN	f (	30 - 37	) IEKFQsEE
12	β -CN	f (	30 - 38	) IEKFQsEEQ
13	β -CN	f (	30 - 39	) IEKFQsEEQQ
14	β -CN	f (	30 - 40	) IEKFQsEEQQQ
15	β -CN	f (	30 - 40	) IEKFqsEEQQQ
16	β -CN	f (	30 - 41	) IEKFQsEEQQQT
17	β -CN	f (	30 - 42	) IEKFQsEEQQQTE
18	β -CN	f (	30 - 43	) IEKFQsEEQQQTED
19	β -CN	f (	30 - 44	) IEKFQsEEQQQTEDE
20	β -CN	f (	30 - 44	) IEKFQsEEqQQTEDE
21	β -CN	f (	30 - 45	) IEKFQsEEQQQTEDEL
22	β -CN	f (	30 - 46	) IEKFQsEEQQQTEDELQ
23	β -CN	f (	30 - 47	) IEKFQsEEQQQTEDELQD
24	β -CN	f (	30 - 48	) IEKFQsEEQQQTEDELQDK
25	β -CN	f (	30 - 51	) IEKFQsEEQQQTEDELQDKIHP
26	β -CN	f (	31 - 43	) EKfQsEEQQQTED
27	β -CN	f (	31 - 44	) EKfQsEEQQQTEDE
28	β -CN	f (	32 - 39	) KfQsEEQQ
29	β -CN	f (	32 - 40	) KfQsEEQQQ
30	β -CN	f (	32 - 42	) KfQsEEQQQTE
31	β -CN	f (	32 - 44	) KfQsEEQQQTEDE
32	β -CN	f (	32 - 45	) KfQsEEQQQTEDEL
33	β -CN	f (	32 - 48	) KfQsEEQQQTEDELQDK
34	β -CN	f (	33 - 38	) FQsEEQ
35	β -CN	f (	33 - 39	) FQsEEQQ
36	β -CN	f (	33 - 40	) FQsEEQQQ
37	β -CN	f (	33 - 41	) FQsEEQQQT
38	β -CN	f (	33 - 42	) FQsEEQQQTE
39	β -CN	f (	33 - 43	) FQsEEQQQTED
40	β -CN	f (	33 - 43	) FQsEEQQqTED
41	β -CN	f (	33 - 44	) FQsEEQQQTEDE
42	β -CN	f (	33 - 44	) FqsEEQQQTEDE
43	β -CN	f (	33 - 45	) FQsEEQQQTEDEL
44	β -CN	f (	33 - 45	) FQsEEqQQTEDEL
45	β -CN	f (	33 - 46	) FQsEEQQQTEDELQ
46	β -CN	f (	33 - 47	) FQsEEQQQTEDELQD
47	β -CN	f (	33 - 48	) FQsEEQQQTEDELQDK
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β -CN	f (	33 - 48	) FQsEEqQQTEDELQDK
β -CN	f (	33 - 51	) FQsEEQQQTEDELQDKIHP
β -CN	f (	33 - 52	) FQsEEQQQTEDELQDKIHPF
β -CN	f (	34 - 44	) QsEEQQQTEDE
β -CN	f (	34 - 45	) QsEEQQQTEDEL
β -CN	f (	34 - 48	) QsEEQQQTEDELQDK
β -CN A1, A2, B	f (	35 - 45	) sEEQQQTEDE
β -CN	f (	35 - 46	) sEEQQQTEDELQ
β -CN	f (	60 - 66	) TEsQSLT

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ict of digesta of **Trentingrana (TN)** at **26 months** of ripening [digestion according the **PePan** protocol]
h CaCl_2 at pH value of:

Modifications	MH+ [Da]	Delta Mass [PPM]	RT [min]	Colo code
S7(Phospho)	1026.486	-0.54	4.8 b	
S7(Phospho); S12(Phospho); S14(Phospho)	2004.749	0.29	8.7 r	
S7(Phospho); S12(Phospho); S14(Phospho)	2247.837	1.04	8.4 r	
S7(Phospho); S12(Phospho); S14(Phospho)	2318.873	0.58	8.9 r	
S7(Phospho); S12(Phospho); S14(Phospho)	2449.914	0.96	9.9 r	
S7(Phospho); S12(Phospho); S14(Phospho)	2578.956	0.39	9.7 r	
S7(Phospho); S12(Phospho); S14(Phospho)	2693.986	1.61	10.2 r	
S6(Phospho)	897.444	0.13	3.5 r	
S6(Phospho); S11(Phospho); S13(Phospho)	2118.793	0.35	8.2 r	
S6(Phospho); S11(Phospho); S13(Phospho)	2189.831	0.78	8.7 r	
S6(Phospho); S11(Phospho); S13(Phospho)	2449.917	1.86	9.4 r	
S6(Phospho); S11(Phospho); S13(Phospho)	2564.941	0.78	10.0 r	
S5(Phospho)	769.349	-0.89	4.1 b	
S5(Phospho)	1054.483	0.98	9.6 n	
N2(Deamidated); S5(Phospho)	1055.467	1.43	9.5 n	
S5(Phospho); S10(Phospho)	1350.524	0.71	8.9 r	
S5(Phospho); S10(Phospho); S12(Phospho)	1747.608	-1.90	8.5 r	
S5(Phospho); S10(Phospho)	1910.732	0.72	8.9 r	
N2(Deamidated); S10(Phospho); S12(Phospho)	1911.716	1.04	8.6 r	
S5(Phospho); S10(Phospho); S12(Phospho)	1990.698	0.56	8.4 r	
S5(Phospho); S10(Phospho); S12(Phospho)	2061.735	0.47	8.8 r	
S5(Phospho); S10(Phospho); S12(Phospho)	2192.777	1.13	10.4 r	
S5(Phospho); S10(Phospho); S12(Phospho)	2321.819	0.80	9.9 r	
S5(Phospho); S10(Phospho); S12(Phospho)	2436.847	1.33	10.3 r	
S5(Phospho); S10(Phospho); S12(Phospho)	2937.124	0.59	15.2 r	
S4(Phospho); S9(Phospho); S11(Phospho)	1891.630	0.94	7.8 r	
S8(Phospho); S10(Phospho)	1697.620	0.32	7.0 r	
S3(Phospho); S8(Phospho); S10(Phospho)	1777.588	1.25	7.1 r	
S7(Phospho); S9(Phospho)	1325.492	0.84	6.4 r	
S7(Phospho); S9(Phospho)	1440.519	0.70	6.4 r	
S9(Phospho)	1488.612	0.87	6.4 r	
S7(Phospho); S9(Phospho)	1568.577	0.03	6.3 r	
S7(Phospho); S9(Phospho); Q13(Deamidated)	1569.565	3.14	6.7 r	
S7(Phospho); S9(Phospho)	1639.615	0.62	7.1 r	
S7(Phospho); S9(Phospho); Q13(Deamidated)	1640.600	1.58	7.4 r	
S2(Phospho); S7(Phospho); S9(Phospho)	1648.544	0.54	5.8 r	
S7(Phospho); S9(Phospho)	1770.655	0.25	8.4 r	

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2	S7(Phospho); S9(Phospho); Q13(Deamidated)	1771.640	0.93	9.3 r
3	S7(Phospho); S9(Phospho)	1899.697	0.17	8.2 r
4	S9(Phospho); T10(Phospho); Q13(Deamidated)	1900.685	2.09	9.1 r
5	S7(Phospho); S9(Phospho); M15(Oxidation)	1915.694	1.29	7.1 r
6	S7(Phospho); S9(Phospho)	2014.724	0.35	8.2 r
7	S7(Phospho); S9(Phospho); Q13(Deamidated)	2015.714	3.19	9.1 r
8	S7(Phospho); S9(Phospho); M15(Oxidation)	2030.721	1.23	7.2 r
9	S7(Phospho); S9(Phospho)	2255.905	0.93	11.5 r
10	S9(Phospho); T10(Phospho)	2383.967	2.32	11.4 r
11	S7(Phospho); S9(Phospho)	2515.003	0.65	14.6 r
12	S6(Phospho); S8(Phospho)	1212.407	0.38	3.4 r
13	S6(Phospho); S8(Phospho)	1455.492	-0.07	4.3 r
14	S6(Phospho); S8(Phospho); Q12(Deamidated)	1456.478	0.76	4.4 r
15	S6(Phospho); S8(Phospho)	1526.530	0.40	5.2 r
16	S1(Phospho); S6(Phospho); S8(Phospho)	1535.457	-0.88	3.1 r
17	S6(Phospho); S8(Phospho)	1657.571	0.68	7.0 r
18	S6(Phospho); S8(Phospho)	1786.613	0.09	6.8 r
19	S6(Phospho); S8(Phospho); M14(Oxidation)	1802.608	0.33	5.7 r
20	S6(Phospho); S8(Phospho)	1901.641	0.80	6.9 r
21	S6(Phospho); S8(Phospho)	2142.822	1.47	9.5 r
22	S6(Phospho); S8(Phospho)	2270.881	1.50	9.3 r
23	S6(Phospho); S8(Phospho)	2401.919	0.72	14.2 r
24	S5(Phospho); S7(Phospho)	1125.376	0.67	3.4 r
25	S5(Phospho); S7(Phospho)	1368.460	-0.13	3.5 r
26	S5(Phospho); S7(Phospho)	1439.498	0.38	5.3 r
27	S5(Phospho); S7(Phospho)	1570.540	1.29	7.1 r
28	S5(Phospho); S7(Phospho)	1814.609	0.67	7.0 r
29	S4(Phospho); S6(Phospho)	997.279	-0.76	3.8 r
30	S4(Phospho); S6(Phospho)	1112.307	0.22	4.0 r
31	S4(Phospho)	1160.400	0.39	5.0 b
32	S4(Phospho); S6(Phospho)	1240.365	-0.28	4.1 r
33	S4(Phospho); S6(Phospho)	1311.404	1.16	5.5 r
34	S4(Phospho); S6(Phospho)	1442.444	0.48	7.5 r
35	S4(Phospho); S6(Phospho)	1571.488	1.34	7.4 r
36	S4(Phospho); S6(Phospho); M12(Oxidation)	1587.482	0.79	5.5 r
37	S4(Phospho); S6(Phospho)	1686.515	1.30	9.5 r
38	S4(Phospho); S6(Phospho)	1927.693	0.52	11.5 r
39	S4(Phospho); S6(Phospho); Q10(Deamidated)	1928.681	2.79	11.8 r
40	S4(Phospho); S6(Phospho); M12(Oxidation)	1943.688	0.87	9.0 r
41	S4(Phospho); S6(Phospho)	2055.751	0.26	11.4 r
42	S4(Phospho); S6(Phospho); M12(Oxidation)	2071.748	1.53	9.1 r
43	S4(Phospho); S6(Phospho)	2186.790	-0.19	13.3 r
44	S4(Phospho); S6(Phospho); M12(Oxidation)	2202.786	0.34	12.4 r
45	S4(Phospho); S6(Phospho)	2315.835	0.61	15.3 r
46	S4(Phospho); S6(Phospho)	2515.915	0.61	16.0 r
47	S3(Phospho); S5(Phospho)	1125.339	0.21	2.8 r
48	S2(Phospho); S4(Phospho)	1012.254	-0.17	3.9 r
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2	S1(Phospho); S3(Phospho)	1157.311	0.28	3.7 r
3	S8(Phospho)	1128.502	1.25	9.7 r
4	S6(Phospho)	887.323	1.22	8.6 b
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6	S3(Phospho); S4(Phospho); S5(Phospho)	1401.464	1.21	10.7 r
7	S2(Phospho); S3(Phospho)	1234.467	2.12	9.5 r
8	S2(Phospho); S3(Phospho); S4(Phospho)	1314.432	1.36	9.8 r
9				
10	S3(Phospho); S4(Phospho); S11(Phospho)	1885.731	2.39	9.6 r
11	S2(Phospho); S3(Phospho); S10(Phospho)	1772.643	0.25	8.8 r
12	S1(Phospho)	954.382	0.42	8.5 n
13	S1(Phospho); S2(Phospho)	1034.349	0.89	8.0 r
14	S1(Phospho); S2(Phospho); N8(Deamidated)	1035.333	0.53	8.8 r
15	S2(Phospho); S9(Phospho)	1605.647	1.23	9.0 r
16	S1(Phospho); S2(Phospho); S9(Phospho)	1685.612	0.36	8.7 r
17	S5(Phospho)	1093.529	-0.32	6.9 n
18				
19	N4(Deamidated); S5(Phospho)	1094.513	0.01	6.7 n
20	S6(Phospho)	1222.572	0.21	8.5 n
21				
22	N5(Deamidated); S6(Phospho)	1223.557	1.41	8.5 n
23	S7(Phospho)	1351.614	-0.35	9.1 n
24	S3(Phospho)	881.377	0.13	8.5 b
25				
26	S12(Phospho)	1537.769	2.01	15.2 n
27	S12(Phospho)	1795.851	-0.11	15.1 n
28	S12(Phospho)	1951.955	1.44	14.3 n
29	S11(Phospho)	1374.705	1.25	14.0 n
30	S11(Phospho)	1632.787	-0.74	13.9 n
31	S11(Phospho)	1788.889	-0.16	13.0 b
32	S10(Phospho)	1660.796	0.86	13.5 n
33				
34	N9(Deamidated); S10(Phospho)	1661.778	-0.03	13.8 n
35	S8(Phospho)	1464.673	-0.13	11.5 n
36	S7(Phospho)	922.429	0.44	11.8 b
37	S7(Phospho)	1180.518	3.80	11.7 b
38	S7(Phospho)	1336.615	0.22	11.2 b
39	N6(Deamidated); S7(Phospho)	1337.598	-0.34	11.4 b
40	S7(Phospho)	1449.700	1.24	13.5 n
41	S6(Phospho)	809.343	-0.82	8.1 b
42	N5(Deamidated); S6(Phospho)	810.328	0.45	8.7 b
43	S6(Phospho)	938.386	-0.45	7.8 n
44				
45	N5(Deamidated); S6(Phospho)	939.372	1.36	8.4 r
46	S6(Phospho)	1067.429	-0.06	8.1 b
47	N5(Deamidated); S6(Phospho)	1068.414	1.07	8.7 b
48	S6(Phospho)	1223.530	0.01	7.6 b
49	N5(Deamidated); S6(Phospho)	1224.514	-0.60	8.2 b
50	S6(Phospho)	1336.616	0.95	12.0 b
51	N5(Deamidated); S6(Phospho)	1337.598	-0.34	12.0 r
52	S6(Phospho)	1473.673	-0.18	9.9 b
53	N5(Deamidated); S6(Phospho)	1474.659	0.89	10.3 r
54	N5(Deamidated); S6(Phospho)	1692.730	0.11	12.0 r
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2	S5(Phospho)	1094.489	1.01	5.9 b
3	N4(Deamidated); S5(Phospho)	1095.472	0.34	6.1 b
4	S4(Phospho)	981.404	-0.26	7.6 b
5	N3(Deamidated); S4(Phospho)	982.386	-1.39	8.0 b
6	S3(Phospho)	726.234	-0.88	8.1 b
7	S3(Phospho)	882.335	-0.29	7.5 b
8				
9	N2(Deamidated); S3(Phospho)	1133.461	-1.52	9.9 n
10	S2(Phospho)	785.282	-0.52	5.7 n
11	S2(Phospho)	1345.567	-3.69	6.9 n
12	S6(Phospho)	880.313	0.25	10.6 n
13	S6(Phospho)	1616.687	-0.46	17.7 n
14	S5(Phospho)	717.250	0.60	9.3 b
15	S9(Phospho)	1566.669	0.62	11.0 n
16	S12(Phospho)	1667.717	0.32	11.2 n
17	T15(Phospho)	2109.943	1.10	15.5 n
18				
19	S8(Phospho); S9(Phospho); S10(Phospho)	1617.495	0.41	5.3 r
20	S2(Phospho); S3(Phospho); S4(Phospho)	964.199	-0.03	2.8 r
21	S1(Phospho); S2(Phospho); S3(Phospho)	865.131	0.74	2.6 r
22	S1(Phospho); S2(Phospho)	811.216	0.40	5.2 r
23	S1(Phospho); S2(Phospho)	1011.334	2.00	9.5 r
24	S4(Phospho)	756.318	0.99	9.4 b
25	S4(Phospho)	857.365	-0.35	10.0 b
26	S3(Phospho)	770.332	-0.97	7.1 n
27	S9(Phospho)	1567.718	-0.46	10.3 n
28	S7(Phospho)	1197.497	0.18	7.5 n
29	S7(Phospho)	1310.581	0.29	11.4 n
30	N1(Deamidated); S7(Phospho)	1311.566	0.37	11.6 n
31	M2(Oxidation); S7(Phospho)	1326.578	1.17	9.4 n
32	S6(Phospho)	1083.455	0.62	7.1 n
33	S6(Phospho)	1196.539	0.49	11.2 n
34	S5(Phospho)	1065.498	0.75	8.9 n
35	N3(Deamidated); S5(Phospho)	1066.483	0.97	9.8 n
36	S3(Phospho)	881.377	0.34	8.9 n
37	S2(Phospho)	767.334	0.18	9.0 n
38	S5(Phospho); S6(Phospho); S9(Phospho)	2078.752	1.44	9.5 r
39	T3(Phospho)	855.385	-0.78	4.8 n
40	S6(Phospho); S8(Phospho)	1352.477	0.17	5.2 r
41	S6(Phospho); S8(Phospho)	1466.519	-0.15	4.3 r
42	S6(Phospho); S8(Phospho)	1553.552	0.30	4.5 r
43	S8(Phospho)	1601.681	0.46	4.7 r
44	S6(Phospho); S8(Phospho)	1681.647	0.35	4.3 b
45	S6(Phospho); S8(Phospho); N11(Deamidated)	1682.630	-0.31	3.9 r
46	S6(Phospho); S8(Phospho)	1809.740	-0.95	3.5 b
47	S6(Phospho); S8(Phospho); N11(Deamidated)	1810.725	-0.22	3.3 r
48	S6(Phospho); S8(Phospho); S12(Phospho)	1889.707	-0.67	3.0 r
49	S6(Phospho); S8(Phospho); N11(Deamidated)	1911.773	0.08	4.6 r
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2	S6(Phospho); S8(Phospho); S12(Phospho)	2881.130	1.85	9.8 r
3	S5(Phospho); S7(Phospho)	1695.699	0.18	3.4 r
4	S6(Phospho)	1331.536	0.10	4.7 b
5	S4(Phospho); S6(Phospho)	1411.502	-0.35	3.8 b
6	S6(Phospho)	1459.630	-0.83	3.7 n
7	S4(Phospho); S6(Phospho)	1539.598	0.31	3.4 b
8	S4(Phospho)	1074.437	1.58	2.7 n
9	S4(Phospho)	1202.530	-0.31	2.2 n
10	S7(Phospho)	1218.496	0.30	9.3 n
11	T8(Phospho)	1218.496	0.36	9.2 r
12	M5(Oxidation); T8(Phospho)	1234.493	1.74	6.2 n
13	T8(Phospho)	1466.613	0.49	12.3 r
14	S7(Phospho)	1466.613	0.57	12.3 n
15	T7(Phospho)	862.291	0.64	6.1 r
16	T7(Phospho)	991.332	-0.61	6.3 n
17	S6(Phospho)	991.332	-0.18	6.3 r
18	T7(Phospho)	1090.400	-0.72	9.6 b
19	M4(Oxidation); S6(Phospho)	1106.396	0.18	6.7 n
20	M4(Oxidation); T7(Phospho)	1106.397	1.02	6.7 r
21	T7(Phospho)	1237.471	0.99	13.7 r
22	S6(Phospho)	1237.471	1.33	13.8 n
23	T7(Phospho)	1338.520	1.78	12.8 b
24	S6(Phospho)	1466.613	0.57	12.0 r
25	S6(Phospho)	1594.708	0.83	11.2 r
26	S4(Phospho)	890.285	-0.18	7.8 n
27	T5(Phospho)	890.286	0.71	9.6 r
28	S3(Phospho)	775.258	0.07	6.4 b
29	S15(Phospho)	1905.921	0.43	17.3 r
30	S14(Phospho)	1749.820	0.08	17.9 r
31	S13(Phospho)	1620.777	0.31	17.6 b
32	S12(Phospho)	1507.693	0.39	16.4 b
33	S11(Phospho)	1378.651	0.78	16.4 r
34	S10(Phospho)	1249.608	0.56	16.1 b
35	S12(Phospho); S13(Phospho); S14(Phospho)	2229.889	1.51	18.0 r
36	S9(Phospho)	1136.524	0.37	14.1 b
37	S7(Phospho)	923.412	-0.43	16.2 b
38	S5(Phospho)	769.339	1.10	11.7 r
39	S6(Phospho); S7(Phospho); S8(Phospho)	1776.675	0.70	10.2 r
40	S3(Phospho); S4(Phospho); S5(Phospho)	1065.250	3.63	5.1 r
41	S3(Phospho); S4(Phospho); S5(Phospho)	1279.380	1.28	9.0 r
42	S3(Phospho); S4(Phospho); S5(Phospho)	1435.480	0.63	7.9 r
43	S2(Phospho); S3(Phospho)	898.248	-0.03	1.9 r
44	S2(Phospho); S3(Phospho); S4(Phospho)	978.214	0.13	1.9 r
45	S2(Phospho); S3(Phospho); S4(Phospho)	1192.347	0.84	7.5 r
46	S2(Phospho); S3(Phospho); S4(Phospho)	1348.448	0.98	6.9 r
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S2(Phospho); S3(Phospho); S4(Phospho)	1461.533	1.51	12.0 r
S1(Phospho); S2(Phospho); S3(Phospho)	865.131	0.74	2.6 r
S1(Phospho); S2(Phospho)	999.296	0.33	5.1 r
S1(Phospho); S2(Phospho); S3(Phospho)	1079.263	0.73	6.5 r
S1(Phospho); S2(Phospho); S3(Phospho)	1235.364	1.14	4.8 r
S1(Phospho); S2(Phospho)	811.216	0.40	5.2 r
S1(Phospho); S2(Phospho)	912.264	0.14	4.7 r
S7(Phospho)	2075.881	0.27	7.5 r
Q6(Deamidated); S7(Phospho)	2076.865	0.33	7.9 r
S6(Phospho)	1089.452	1.75	7.2 r
S6(Phospho)	1217.508	-0.33	6.9 n
S6(Phospho)	1345.567	-0.19	6.8 b
S6(Phospho)	1473.626	0.08	6.9 b
Q5(Deamidated); S6(Phospho)	1474.607	-1.66	7.3 b
S6(Phospho)	1574.672	-0.90	7.3 n
S6(Phospho)	1703.716	-0.26	7.4 b
S6(Phospho)	1818.742	-0.29	7.5 b
S6(Phospho)	1947.784	-0.65	7.8 b
S6(Phospho); Q9(Deamidated)	1948.774	2.23	8.1 r
S6(Phospho)	2060.869	-0.48	11.0 b
S6(Phospho)	2188.930	1.01	9.4 b
S6(Phospho)	2303.964	3.99	9.4 r
S6(Phospho)	2432.051	0.37	9.9 b
S6(Phospho)	2779.249	1.04	11.1 n
S5(Phospho)	1705.660	0.52	6.0 n
S5(Phospho)	1834.703	0.96	6.7 r
S4(Phospho)	1103.440	-0.05	3.5 n
S4(Phospho)	1231.497	-1.32	3.7 n
S4(Phospho)	1461.589	0.01	5.3 b
S4(Phospho)	1705.660	0.52	6.0 b
S4(Phospho)	1818.743	-0.23	10.0 b
S4(Phospho)	2189.926	0.95	9.0 n
S3(Phospho)	847.287	0.22	2.9 b
S3(Phospho)	975.346	-0.04	3.0 b
S3(Phospho)	1103.404	-0.37	3.0 b
S3(Phospho)	1204.452	0.51	4.3 n
S3(Phospho)	1333.494	-0.45	4.8 b
S3(Phospho)	1448.521	-0.31	4.9 b
S3(Phospho); Q8(Deamidated)	1449.507	0.86	5.5 r
S3(Phospho)	1577.563	-0.59	5.7 b
Q2(Deamidated); S3(Phospho)	1578.549	0.41	6.4 r
S3(Phospho)	1690.648	-0.03	10.2 b
S3(Phospho); Q6(Deamidated)	1691.633	0.83	10.5 r
S3(Phospho)	1818.706	-0.08	9.1 b
S3(Phospho)	1933.735	0.57	9.2 r
S3(Phospho)	2061.828	-0.06	9.1 b

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2	S3(Phospho); Q6(Deamidated)	2062.814	0.47	9.8 r
3	S3(Phospho)	2409.023	-0.44	12.2 b
4	S3(Phospho)	2556.092	-0.34	14.8 b
5	S2(Phospho)	1430.496	0.07	2.1 r
6	S2(Phospho)	1543.580	0.09	8.3 n
7	S2(Phospho)	1914.760	-0.23	7.3 n
8	S1(Phospho)	1302.437	0.35	2.0 r
9	S1(Phospho)	1543.580	0.25	8.4 n
10	S3(Phospho)	845.330	1.39	5.1 n
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For Peer Review

Number of phosphorylated serine residues per peptide	Number of phosphorylated threonine residues per peptide	Number of phosphorylated residues per peptides
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Peptide length	Max peptide length	Min peptide length
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Supplementary Table S2. TN_13_COST. Caseinophosphopeptides release
 CPPs isolated from cheese digesta by selective precipitation
 pH 8.0 are indicated in black;
 pH 4.6 are indicated in red;
 both, pH 8.0 and pH 4.6, are indicated in blue.

Protein fragment	Sequence
α S1-CN f (35 - 42)	EKVNELsK
α S1-CN f (37 - 42)	VNELsK
α S1-CN f (37 - 52)	VNELsKDIGsEsTEDQ
α S1-CN f (40 - 52)	LSKDIGsEsTEDQ
α S1-CN f (41 - 52)	SKDIGsEsTEDQ
α S1-CN f (41 - 53)	SKDIGsEsTEDQA
α S1-CN f (41 - 52)	sKDIGsEsTEDQ
α S1-CN f (41 - 54)	SKDIGsEsTEDQAM
α S1-CN f (42 - 52)	KDIGsEsTEDQ
α S1-CN f (42 - 53)	KDIGsEsTEDQA
α S1-CN f (43 - 50)	DIGsEsTE
α S1-CN f (43 - 51)	DIGsEsTED
α S1-CN f (43 - 52)	DIGsESTEDQ
α S1-CN f (43 - 52)	DIGsEsTEDQ
α S1-CN f (43 - 53)	DIGsEsTEDQA
α S1-CN f (43 - 53)	DIGsEsTEDqA
α S1-CN f (43 - 54)	DIGsESTEDQAM
α S1-CN f (43 - 54)	DIGsEsTEDQAM
α S1-CN f (43 - 55)	DIGsEsTEDQAME
α S1-CN f (43 - 55)	DIGsEsTEDQAmE
α S1-CN f (43 - 56)	DIGsEsTEDQAmED
α S1-CN f (43 - 57)	DIGsEsTEDQAmEDI
α S1-CN f (43 - 58)	DIGsEsTEDQAMEDIK
α S1-CN f (43 - 58)	DIGsEsTEDqAMEDIK
α S1-CN f (43 - 58)	DIGsEsTEDQAmEDIK
α S1-CN f (43 - 58)	DIGsEstEDQAMEDIK
α S1-CN f (44 - 52)	IGsEsTEDQ
α S1-CN f (45 - 52)	GsEsTEDQ
α S1-CN f (59 - 65)	QMEAEsI
α S1-CN f (59 - 74)	QMEAEsIssSEEIVPN
α S1-CN f (60 - 65)	MEAEsI
α S1-CN f (61 - 74)	EAEsIssSEEIVPN
α S1-CN f (64 - 74)	slssSEEIVPN
α S1-CN f (65 - 74)	IsssEEIVPN
α S1-CN f (66 - 74)	SssEEIVPN
α S1-CN f (66 - 74)	sssEEIVPN
α S1-CN f (66 - 78)	ssEEIVPNsVEQ

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2	α S1-CN	f (	67 - 72	) SsEEIV
3	α S1-CN	f (	67 - 74	) sSEEIVPN
4	α S1-CN	f (	67 - 74	) SsEEIVPN
5	α S1-CN	f (	67 - 74	) ssEEIVPN
6	α S1-CN	f (	67 - 74	) ssEEIVPn
7	α S1-CN	f (	67 - 74	) ssEEIVPn
8	α S1-CN	f (	68 - 74	) sEEIVPN
9	α S1-CN	f (	70 - 78	) EIVPNsVEQ
10	α S1-CN	f (	73 - 78	) PNsVEQ
11	α S1-CN	f (	73 - 79	) PNsVEQK
12	α S1-CN	f (	73 - 79	) PNsVEQK
13	α S1-CN	f (	105 - 118	) KVPQLEIVPNsAEE
14	α S1-CN	f (	106 - 118	) VPQLEIVPNsAEE
15	α S1-CN	f (	106 - 119	) VPQLEIVPNsAEER
16	α S1-CN	f (	106 - 119	) VPQLEIVPNsAEER
17	α S1-CN	f (	106 - 119	) VPQLEIVPNsAEER
18	α S1-CN	f (	109 - 116	) LEIVPNsA
19	α S1-CN	f (	109 - 118	) LEIVPNsAEE
20	α S1-CN	f (	109 - 118	) LEIVPNsAEE
21	α S1-CN	f (	109 - 118	) LEIVPNsAEE
22	α S1-CN	f (	109 - 119	) LEIVPNsAEER
23	α S1-CN	f (	109 - 119	) LEIVPNsAEER
24	α S1-CN	f (	110 - 116	) EIVPNsA
25	α S1-CN	f (	110 - 116	) EIVPNsA
26	α S1-CN	f (	110 - 116	) EIVPNsA
27	α S1-CN	f (	110 - 117	) EIVPNsAE
28	α S1-CN	f (	110 - 117	) EIVPNsAE
29	α S1-CN	f (	110 - 118	) EIVPNsAEE
30	α S1-CN	f (	110 - 118	) EIVPNsAEE
31	α S1-CN	f (	110 - 118	) EIVPNsAEE
32	α S1-CN	f (	110 - 119	) EIVPNsAEER
33	α S1-CN	f (	110 - 119	) EIVPNsAEER
34	α S1-CN	f (	111 - 119	) IVPNsAEER
35	α S1-CN	f (	111 - 119	) IVPNsAEER
36	α S1-CN	f (	112 - 118	) VPNsAEE
37	α S1-CN	f (	112 - 119	) VPNsAEER
38	α S1-CN	f (	112 - 119	) VPNsAEER
39	α S1-CN	f (	112 - 119	) VPNsAEER
40	α S1-CN	f (	113 - 118	) PNsAEE
41	α S1-CN	f (	113 - 118	) PnsAEE
42	α S1-CN	f (	113 - 118	) PnsAEE
43	α S1-CN	f (	113 - 119	) PNsAEER
44	α S1-CN	f (	173 - 186	) YTDAPSFsDIPNPI
45	α S1-CN	f (	174 - 186	) TDAPsFSDIPNPI
46	α S1-CN	f (	180 - 190	) SDIPNPIGsEN
47	α S1-CN	f (	180 - 190	) SDIPNPIGsEN
48	α S1-CN	f (	180 - 193	) SDIPNPIGsENSEK
49	α S2-CN	f (	5 - 15	) EHVsssEESII
50	α S2-CN	f (	6 - 15	) HVsssEESII
51	α S2-CN	f (	6 - 15	) HVsssEESII
52	α S2-CN	f (	7 - 13	) VsssEES
53	α S2-CN	f (	7 - 13	) VsssEES
54	α S2-CN	f (	7 - 15	) VsssEESII
55	α S2-CN	f (	8 - 14	) ssSEESI
56	α S2-CN	f (	8 - 14	) sssEESI
57	α S2-CN	f (	8 - 14	) sssEESI
58	α S2-CN	f (	9 - 14	) ssEESI
59	α S2-CN	f (	9 - 15	) ssEESII
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2	α S2-CN	f (	9 - 16	) ssEEsIIS
3	α S2-CN	f (	9 - 17	) ssEEsIISQ
4	α S2-CN	f (	9 - 18	) ssEEsIISQE
5	α S2-CN	f (	13 - 18	) SIIsQE
6	α S2-CN	f (	13 - 19	) SIIsQET
7	α S2-CN	f (	14 - 19	) IIsQET
8	α S2-CN	f (	25 - 33	) NMAINPsK
9	α S2-CN	f (	25 - 33	) NMAINPsKE
10	α S2-CN	f (	25 - 33	) nMAINPsKE
11	α S2-CN	f (	25 - 33	) NmAINPsKE
12	α S2-CN	f (	25 - 34	) NMAINPsKEN
13	α S2-CN	f (	25 - 35	) NMAINPsKENL
14	α S2-CN	f (	25 - 35	) NMAInPsKENL
15	α S2-CN	f (	25 - 35	) NmAINPsKENL
16	α S2-CN	f (	26 - 34	) MAINPsKEN
17	α S2-CN	f (	26 - 35	) MAINPsKENL
18	α S2-CN	f (	27 - 32	) AINPsK
19	α S2-CN	f (	27 - 35	) AINPsKENL
20	α S2-CN	f (	29 - 35	) NPsKENL
21	α S2-CN	f (	53 - 60	) SIGsssEE
22	α S2-CN	f (	53 - 65	) SIGSssEEsAEVA
23	α S2-CN	f (	56 - 65	) sssEEsAEVA
24	α S2-CN	f (	63 - 69	) EVAtEEV
25	α S2-CN	f (	64 - 69	) VAtEEV
26	α S2-CN	f (	124 - 133	) NREQLStsEE
27	α S2-CN	f (	124 - 133	) NREqLStsEE
28	α S2-CN	f (	126 - 133	) EQLStsEE
29	α S2-CN	f (	126 - 133	) EQLStsEE
30	α S2-CN	f (	126 - 135	) EQLsTsEENS
31	α S2-CN	f (	126 - 136	) EQLsTsEENSK
32	α S2-CN	f (	126 - 136	) EQLsTsEEnSK
33	α S2-CN	f (	126 - 136	) EQLsTsEENsK
34	α S2-CN	f (	126 - 136	) EQLsTsEENsKK
35	α S2-CN	f (	128 - 135	) LsTsEENS
36	α S2-CN	f (	137 - 146	) KTVDMesTEV
37	α S2-CN	f (	137 - 146	) KTVDMEstEV
38	α S2-CN	f (	138 - 144	) TVDMesT
39	α S2-CN	f (	138 - 145	) TVDMEstE
40	α S2-CN	f (	138 - 146	) TVDMesTEV
41	α S2-CN	f (	138 - 146	) TVDMEstEV
42	α S2-CN	f (	138 - 146	) TVDMesTEV
43	α S2-CN	f (	138 - 146	) TVDMEstEV
44	α S2-CN	f (	138 - 146	) tVDMesTEV
45	α S2-CN	f (	139 - 146	) VDMEstEV
46	α S2-CN	f (	139 - 146	) VDMesTEV
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2	α S2-CN	f (	140 - 146	) DMEsTEV
3	α S2-CN	f (	141 - 146	) MEsTEV
4	β -CN	f (	3 - 16	) LEELNVPGEIVeSL
5	β -CN	f (	4 - 16	) EELNVPGEIVeSL
6	β -CN	f (	6 - 16	) LNVPGEIVeSL
7	β -CN	f (	7 - 16	) NVPGEIVeSL
8	β -CN	f (	7 - 24	) NVPGEIVeSLssSEESIT
9	β -CN	f (	8 - 16	) VPGEIVeSL
10	β -CN	f (	9 - 16	) PGEIVeSL
11	β -CN	f (	10 - 16	) GEIVeSL
12	β -CN	f (	11 - 16	) EIVeSL
13	β -CN	f (	15 - 22	) SLssssEES
14	β -CN	f (	15 - 24	) SLssssEESIT
15	β -CN	f (	16 - 22	) LssssEES
16	β -CN	f (	16 - 23	) LssssEESI
17	β -CN	f (	16 - 24	) LSssEESIT
18	β -CN	f (	16 - 24	) LssssEESIT
19	β -CN	f (	17 - 23	) ssSEESI
20	β -CN	f (	17 - 23	) sssEESI
21	β -CN	f (	17 - 24	) ssSEESIT
22	β -CN	f (	17 - 24	) sssEESIT
23	β -CN	f (	18 - 23	) ssEESI
24	β -CN	f (	18 - 24	) SsEESIT
25	β -CN	f (	18 - 24	) ssEESIT
26	β -CN	f (	32 - 40	) KFQsEEQQQ
27	β -CN	f (	32 - 45	) KFQsEEQQQTEDEL
28	β -CN	f (	33 - 38	) FQsEEQ
29	β -CN	f (	33 - 39	) FQsEEQQ
30	β -CN	f (	33 - 40	) FQsEEQQQ
31	β -CN	f (	33 - 40	) FQsEEQqQ
32	β -CN	f (	33 - 41	) FQsEEQQQT
33	β -CN	f (	33 - 44	) FQsEEQQQTEDE
34	β -CN	f (	33 - 44	) FQsEEQQqTEDE
35	β -CN	f (	33 - 45	) FQsEEQQQTEDEL
36	β -CN	f (	33 - 45	) FQsEEqQQTEDEL
37	β -CN	f (	33 - 46	) FQsEEQQQTEDELQ
38	β -CN	f (	33 - 47	) FQsEEQQQTEDELQD
39	β -CN	f (	33 - 48	) FQsEEQQQTEDELQDK
40	β -CN	f (	33 - 48	) FQsEEQQqTEDELQDK
41	β -CN	f (	33 - 51	) FQsEEQQQTEDELQDKIHP
42	β -CN	f (	34 - 45	) QsEEQQQTEDEL
43	κ -CN	f (	153 - 165	) IESPPEINTVqVt
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and after digestion according the protocol of Minekus et al. (2014) of Trentingrana cheese at 13 months of ripening with CaCl_2 at pH value of:

Modifications	MH+ [Da]	Delta Mass [PPM]	RT [min]	Color code
S7(Phospho)	1026.486	-0.73	4.6 b	
S5(Phospho)	769.348	-1.04	3.8 b	
S5(Phospho); S10(Phospho); S12(Phospho)	1990.695	-1.10	8.1 r	
S7(Phospho); S9(Phospho)	1568.575	-0.98	6.2 r	
S6(Phospho); S8(Phospho)	1455.490	-1.50	3.5 r	
S6(Phospho); S8(Phospho)	1526.527	-1.76	5.3 r	
S1(Phospho); S6(Phospho); S8(Phospho)	1535.457	-1.20	2.7 r	
S6(Phospho); S8(Phospho)	1657.568	-1.08	7.0 r	
S5(Phospho); S7(Phospho)	1368.459	-1.38	3.3 r	
S5(Phospho); S7(Phospho)	1439.502	2.84	5.3 r	
S4(Phospho); S6(Phospho)	997.278	-1.80	3.3 r	
S4(Phospho); S6(Phospho)	1112.305	-1.54	3.4 r	
S4(Phospho)	1160.399	-0.24	5.0 b	
S4(Phospho); S6(Phospho)	1240.363	-1.66	3.6 r	
S4(Phospho); S6(Phospho)	1311.401	-1.21	5.5 r	
S4(Phospho); S6(Phospho); Q10(Deamidated)	1312.387	0.03	5.9 r	
S4(Phospho)	1362.475	-1.09	7.7 n	
S4(Phospho); S6(Phospho)	1442.442	-0.71	7.4 r	
S4(Phospho); S6(Phospho)	1571.483	-1.58	7.1 r	
S4(Phospho); S6(Phospho); M12(Oxidation)	1587.480	-0.36	5.9 r	
S4(Phospho); S6(Phospho); M12(Oxidation)	1702.506	-1.11	6.0 r	
S4(Phospho); S6(Phospho); M12(Oxidation)	1815.590	-1.09	10.0 r	
S4(Phospho); S6(Phospho)	1927.689	-1.32	11.6 r	
S4(Phospho); S6(Phospho); Q10(Deamidated)	1928.674	-0.81	11.8 r	
S4(Phospho); S6(Phospho); M12(Oxidation)	1943.684	-1.26	9.1 r	
S4(Phospho); S6(Phospho); T7(Phospho)	2007.656	-1.21	11.0 r	
S3(Phospho); S5(Phospho)	1125.337	-1.20	2.8 r	
S2(Phospho); S4(Phospho)	1012.252	-2.10	3.8 r	
S6(Phospho)	887.321	-0.36	8.6 b	
S6(Phospho); S8(Phospho); S9(Phospho)	1989.682	-0.88	11.5 r	
S5(Phospho)	759.263	-0.68	8.5 b	
S4(Phospho); S6(Phospho); S7(Phospho)	1730.584	-0.55	9.8 r	
S1(Phospho); S3(Phospho); S4(Phospho)	1401.462	-0.50	9.5 r	
S2(Phospho); S3(Phospho); S4(Phospho)	1314.430	-0.59	8.8 r	
S2(Phospho); S3(Phospho)	1121.379	-1.18	8.2 r	
S1(Phospho); S2(Phospho); S3(Phospho)	1201.346	-0.51	7.9 r	
S1(Phospho); S2(Phospho); S9(Phospho)	1557.514	-1.49	8.7 r	

1				
2	S2(Phospho)	743.286	-0.05	8.6 n
3	S1(Phospho)	954.381	-0.86	8.5 r
4	S2(Phospho)	954.381	-0.74	8.5 n
5	S1(Phospho); S2(Phospho)	1034.347	-0.88	7.9 r
6	S1(Phospho); S2(Phospho); N8(Deamidated)	1035.331	-0.77	8.8 r
7	S1(Phospho)	867.349	-0.54	8.6 n
8	S6(Phospho)	1094.476	-0.81	9.1 n
9	S3(Phospho)	753.281	-1.15	9.1 n
10	S3(Phospho)	881.376	-0.42	8.9 n
11	S11(Phospho)	1632.787	-0.74	13.8 n
12	S10(Phospho)	1504.692	-0.89	14.0 n
13	S10(Phospho)	1660.792	-1.12	13.5 n
14	N9(Deamidated); S10(Phospho)	1661.777	-0.76	13.8 n
15	S7(Phospho)	922.428	-0.29	11.8 n
16	S7(Phospho)	1180.512	-0.96	11.6 b
17	N6(Deamidated); S7(Phospho)	1181.498	0.18	12.3 b
18	S7(Phospho)	1336.615	0.04	11.0 b
19	N6(Deamidated); S7(Phospho)	1337.597	-0.97	11.4 b
20	S6(Phospho)	809.343	-1.43	8.1 n
21	N5(Deamidated); S6(Phospho)	810.327	-1.13	8.7 n
22	S6(Phospho)	938.386	-0.97	7.8 r
23	N5(Deamidated); S6(Phospho)	939.369	-1.37	8.4 r
24	S6(Phospho)	1067.428	-1.32	8.1 b
25	N5(Deamidated); S6(Phospho)	1068.413	-0.64	8.6 b
26	S6(Phospho)	1223.529	-0.99	7.6 b
27	N5(Deamidated); S6(Phospho)	1224.513	-1.09	8.1 b
28	S5(Phospho)	1094.488	-0.10	5.7 b
29	N4(Deamidated); S5(Phospho)	1095.469	-2.23	6.1 n
30	S4(Phospho)	825.301	-1.74	11.7 n
31	S4(Phospho)	981.401	-2.38	7.6 n
32	N3(Deamidated); S4(Phospho)	982.386	-1.64	8.0 n
33	S3(Phospho)	726.233	-1.30	8.1 b
34	N2(Deamidated); S3(Phospho)	727.217	-2.15	8.6 b
35	S3(Phospho)	882.334	-1.26	7.6 n
36	S8(Phospho)	1616.687	-0.54	16.8 n
37	S5(Phospho)	1453.624	-0.79	16.5 n
38	S9(Phospho)	1222.498	-0.27	11.5 n
39	S9(Phospho)	1566.667	-1.10	11.0 n
40	S4(Phospho); S5(Phospho); S6(Phospho)	1456.466	-1.37	10.6 r
41	S3(Phospho); S4(Phospho); S5(Phospho)	1327.424	-1.32	10.6 r
42	S2(Phospho); S3(Phospho); S4(Phospho)	964.198	-0.60	1.9 r
43	S2(Phospho); S3(Phospho); S4(Phospho)	1190.365	-1.41	10.6 r
44	S1(Phospho); S2(Phospho)	898.247	-0.98	5.3 r
45	S1(Phospho); S2(Phospho); S3(Phospho)	978.214	-0.49	5.4 r
46	S1(Phospho); S2(Phospho)	811.215	-1.11	5.2 r
47	S1(Phospho); S2(Phospho)	924.299	-0.73	10.5 r
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2	S1(Phospho); S2(Phospho); S5(Phospho)	1091.297	-0.74	7.1 r
3	S1(Phospho); S2(Phospho); S5(Phospho)	1219.356	-0.35	7.5 r
4	S1(Phospho); S2(Phospho); S5(Phospho)	1348.399	-0.50	8.2 r
5	S4(Phospho)	756.318	0.18	9.3 b
6	S4(Phospho)	857.365	-0.21	10.0 b
7	S3(Phospho)	770.333	-0.65	7.0 n
8	S7(Phospho)	954.410	-1.78	7.1 n
9	S7(Phospho)	1083.453	-1.19	8.1 n
10	N1(Deamidated); S7(Phospho)	1084.437	-0.97	8.2 n
11	M2(Oxidation); S7(Phospho)	1099.449	0.24	5.5 n
12	S7(Phospho)	1197.495	-1.35	7.4 n
13	S7(Phospho)	1310.580	-0.83	11.4 n
14	N5(Deamidated); S7(Phospho)	1311.565	0.28	12.3 n
15	M2(Oxidation); S7(Phospho)	1326.576	0.07	9.4 n
16	S6(Phospho)	1083.454	-0.17	7.0 n
17	S6(Phospho)	1196.538	-0.53	11.2 n
18	S5(Phospho)	709.327	-1.12	2.4 n
19	S5(Phospho)	1065.498	0.41	8.9 b
20	N3(Deamidated); S5(Phospho)	1066.482	0.28	9.8 n
21	S3(Phospho)	881.376	-0.84	8.9 n
22	S4(Phospho); S5(Phospho); S6(Phospho)	1035.235	-0.92	3.1 r
23	S5(Phospho); S6(Phospho); S9(Phospho)	1492.452	-0.86	7.0 r
24	S1(Phospho); S2(Phospho); S3(Phospho)	1235.314	-1.07	3.2 r
25	T4(Phospho)	856.333	-0.56	7.6 r
26	T3(Phospho)	727.291	-0.67	6.5 b
27	T7(Phospho); S8(Phospho)	1352.476	-0.82	5.1 r
28	Q4(Deamidated); T7(Phospho); S8(Phospho)	1353.461	-0.19	5.7 r
29	S6(Phospho)	1002.365	-1.25	5.7 r
30	T5(Phospho); S6(Phospho)	1082.331	-1.51	4.2 r
31	S4(Phospho); S6(Phospho)	1283.406	-1.15	3.2 r
32	S4(Phospho); S6(Phospho)	1411.501	-1.39	3.7 r
33	S4(Phospho); S6(Phospho); N9(Deamidated)	1412.485	-1.22	3.2 r
34	S4(Phospho); S6(Phospho); S10(Phospho)	1491.467	-1.41	2.8 r
35	S4(Phospho); S6(Phospho); S10(Phospho)	1619.562	-1.30	3.0 r
36	S2(Phospho); S4(Phospho)	1026.306	-0.27	2.4 r
37	S7(Phospho)	1218.495	-1.20	9.2 b
38	M5(Oxidation); T8(Phospho)	1234.490	-0.53	6.4 n
39	S6(Phospho)	862.290	0.43	6.0 b
40	T7(Phospho)	991.334	1.12	6.3 b
41	S6(Phospho)	1090.399	-2.29	9.6 n
42	T7(Phospho)	1090.400	-0.83	9.6 r
43	M4(Oxidation); S6(Phospho)	1106.395	-1.19	6.6 r
44	M4(Oxidation); T7(Phospho)	1106.396	-0.37	6.6 n
45	T1(Phospho); S6(Phospho)	1170.367	-0.38	9.0 r
46	T6(Phospho)	989.353	-0.66	9.4 r
47	S5(Phospho)	989.353	-0.04	9.4 n
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2	S4(Phospho)	890.284	-1.55	9.2 b
3	S3(Phospho)	775.258	-0.56	6.4 b
4	S13(Phospho)	1620.775	-1.05	17.6 r
5	S12(Phospho)	1507.693	0.06	16.5 b
6	S10(Phospho)	1249.607	-0.61	16.2 b
7	S9(Phospho)	1136.523	-0.92	14.3 b
8	S9(Phospho); S11(Phospho); S12(Phospho)	2116.800	-0.68	14.3 r
9	S8(Phospho)	1022.480	-0.39	13.6 b
10	S7(Phospho)	923.411	-1.22	16.5 b
11	S6(Phospho)	826.359	-0.66	12.2 b
12	S5(Phospho)	769.337	-1.20	11.7 b
13	S3(Phospho); S4(Phospho); S5(Phospho)	1065.246	-0.38	2.8 r
14	S3(Phospho); S4(Phospho); S5(Phospho)	1279.377	-0.78	7.8 r
15	S2(Phospho); S3(Phospho); S4(Phospho)	978.214	-0.24	1.9 r
16	S2(Phospho); S3(Phospho); S4(Phospho)	1091.297	-0.96	7.3 r
17	S3(Phospho); S4(Phospho)	1112.379	-0.99	7.5 r
18	S2(Phospho); S3(Phospho); S4(Phospho)	1192.346	-0.23	6.6 r
19	S1(Phospho); S2(Phospho)	898.247	-0.98	5.3 r
20	S1(Phospho); S2(Phospho); S3(Phospho)	978.214	-0.49	5.4 r
21	S1(Phospho); S2(Phospho)	999.295	-0.96	5.1 r
22	S1(Phospho); S2(Phospho); S3(Phospho)	1079.261	-0.62	6.3 r
23	S1(Phospho); S2(Phospho)	811.215	-1.11	5.2 r
24	S2(Phospho)	832.295	-2.24	5.3 n
25	S1(Phospho); S2(Phospho)	912.263	-1.06	4.6 r
26	S4(Phospho)	1231.499	-0.43	3.8 n
27	S4(Phospho)	1818.741	-1.23	10.0 n
28	S3(Phospho)	847.285	-1.79	2.6 b
29	S3(Phospho)	975.343	-2.23	2.9 b
30	S3(Phospho)	1103.403	-1.14	3.1 b
31	S3(Phospho); Q7(Deamidated)	1104.388	0.29	3.7 n
32	S3(Phospho)	1204.451	-0.80	4.3 n
33	S3(Phospho)	1577.563	-0.44	5.5 b
34	S3(Phospho); Q8(Deamidated)	1578.547	-0.68	6.1 r
35	S3(Phospho)	1690.646	-0.97	10.2 b
36	S3(Phospho); Q6(Deamidated)	1691.632	-0.25	10.6 n
37	S3(Phospho)	1818.705	-1.09	9.1 n
38	S3(Phospho)	1933.731	-1.33	9.2 r
39	S3(Phospho)	2061.827	-0.77	8.4 b
40	S3(Phospho); Q8(Deamidated)	2062.817	2.01	9.5 n
41	S3(Phospho)	2409.023	-0.44	10.8 n
42	S2(Phospho)	1543.579	-0.23	8.3 n
43	Q11(Deamidated); T13(Phospho)	1507.692	-0.82	16.4 b
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Number of phosphorylated serine residues per peptide	Number of phosphorylated threonine residues per peptide	Number of phosphorylated residues per peptides
1	0	1
1	0	1
3	0	3
2	0	2
2	0	2
2	0	2
3	0	3
2	0	2
2	0	2
2	0	2
2	0	2
2	0	2
1	0	1
2	0	2
2	0	2
2	0	2
1	0	1
2	0	2
2	0	2
2	0	2
2	0	2
2	0	2
2	0	2
2	0	2
2	0	2
2	0	2
2	0	2
2	1	3
2	0	2
2	0	2
1	0	1
3	0	3
1	0	1
3	0	3
3	0	3
3	0	3
2	0	2
3	0	3
3	0	3

1			
2	1	0	1
3	1	0	1
4	1	0	1
5	2	0	2
6	2	0	2
7	1	0	1
8	1	0	1
9	1	0	1
10	1	0	1
11	1	0	1
12	1	0	1
13	1	0	1
14	1	0	1
15	1	0	1
16	1	0	1
17	1	0	1
18	1	0	1
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36	1	0	1
37	1	0	1
38	1	0	1
39	1	0	1
40	1	0	1
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42	1	0	1
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44	1	0	1
45	1	0	1
46	1	0	1
47	1	0	1
48	1	0	1
49	3	0	3
50	3	0	3
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52	3	0	3
53	3	0	3
54	2	0	2
55	3	0	3
56	2	0	2
57	2	0	2
58	2	0	2
59	2	0	2
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2	3	0	3
3	3	0	3
4	3	0	3
5	1	0	1
6	1	0	1
7	1	0	1
8	1	0	1
9	1	0	1
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14	1	0	1
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23	1	0	1
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25	1	0	1
26	1	0	1
27	3	0	3
28	3	0	3
29	3	0	3
30	3	0	3
31	0	1	1
32	0	1	1
33	1	1	2
34	1	1	2
35	1	0	1
36	1	1	2
37	2	0	2
38	2	0	2
39	2	0	2
40	2	0	2
41	3	0	3
42	3	0	3
43	2	0	2
44	1	0	1
45	0	1	1
46	1	0	1
47	0	1	1
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49	0	1	1
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51	0	1	1
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53	0	1	1
54	1	0	1
55	0	1	1
56	1	1	2
57	0	1	1
58	1	0	1
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4	1	0	1
5	1	0	1
6	1	0	1
7	1	0	1
8	1	0	1
9	3	0	3
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13	1	0	1
14	1	0	1
15	3	0	3
16	3	0	3
17	3	0	3
18	3	0	3
19	3	0	3
20	3	0	3
21	2	0	2
22	3	0	3
23	2	0	2
24	3	0	3
25	2	0	2
26	3	0	3
27	2	0	2
28	3	0	3
29	2	0	2
30	1	0	1
31	2	0	2
32	1	0	1
33	1	0	1
34	1	0	1
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36	1	0	1
37	1	0	1
38	1	0	1
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41	1	0	1
42	1	0	1
43	1	0	1
44	1	0	1
45	1	0	1
46	1	0	1
47	1	0	1
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49	1	0	1
50	1	0	1
51	1	0	1
52	1	0	1
53	1	0	1
54	0	1	1
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Peptide length	Max peptide length	Min peptide length
8	19	6

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19	10
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27	9
28	10
29	10
30	9
31	9
32	7
33	8
34	8
35	6
36	6
37	7
38	14
39	13
40	11
41	14
42	11
43	10
44	7
45	9
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48	6
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For Peer Review

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26 13
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32 8
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35 11
36 11
37 11
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42 7
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For Peer Review

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2	7
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For Peer Review

Supplementary Table S2. TN_19_COST. Caseinophosphopeptides released from CPPs isolated from cheese digesta by selective precipitation at pH 8.0 are indicated in black; pH 4.6 are indicated in red; both, pH 8.0 and pH 4.6, are indicated in blue.

Protein fragment	Sequence
α S1-CN f (35 - 42)	EKVNELsK
α S1-CN f (35 - 42)	EKVnELsK
α S1-CN f (37 - 42)	VNELsK
α S1-CN f (37 - 42)	VnELsK
α S1-CN f (37 - 52)	VNELsKDIGsEsTEDQ
α S1-CN f (40 - 50)	LSKDIGsEsTE
α S1-CN f (40 - 51)	LSKDIGsEsTED
α S1-CN f (40 - 52)	LSKDIGsEsTEDQ
α S1-CN f (41 - 52)	SKDIGsEsTEDQ
α S1-CN f (41 - 52)	sKDIGsEsTEDQ
α S1-CN f (41 - 54)	SKDIGsEsTEDQAM
α S1-CN f (42 - 54)	KDIGsEsTEDQ
α S1-CN f (42 - 56)	KDIGsEsTEDQAM
α S1-CN f (43 - 50)	DIGsEsTE
α S1-CN f (43 - 51)	DIGsESTED
α S1-CN f (43 - 51)	DIGsEsTED
α S1-CN f (43 - 52)	DIGsESTEDQ
α S1-CN f (43 - 52)	DIGsEsTEDQ
α S1-CN f (43 - 53)	DIGsEsTEDQA
α S1-CN f (43 - 53)	DIGsEsTEDqA
α S1-CN f (43 - 54)	DIGsEsTEDQAM
α S1-CN f (43 - 56)	DIGsEsTEDQAmED
α S1-CN f (43 - 58)	DIGsEsTEDQAMEDIK
α S1-CN f (43 - 58)	DIGsEsTEDqAMEDIK
α S1-CN f (43 - 58)	DIGsEsTEDQAmEDIK
α S1-CN f (43 - 58)	DIGsEstEDQAMEDIK
α S1-CN f (44 - 52)	IGsEsTEDQ
α S1-CN f (45 - 52)	GsEsTEDQ
α S1-CN f (59 - 65)	QMEAEsl
α S1-CN f (59 - 74)	QMEAEslsSEEIVPN
α S1-CN f (60 - 65)	MEAEsl
α S1-CN f (61 - 74)	EAEslsSEEIVPN
α S1-CN f (64 - 74)	SIssEEIVPN
α S1-CN f (65 - 74)	IssEEIVPN
α S1-CN f (66 - 74)	ssSEEIVPN
α S1-CN f (66 - 74)	sssEEIVPN
α S1-CN f (67 - 72)	ssEEIV
α S1-CN f (67 - 74)	sSEEIVPN
α S1-CN f (67 - 74)	ssEEIVPN
α S1-CN f (67 - 74)	ssEEIVPn

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2	α S1-CN	f (	73 - 79	) PNsVEQK
3	α S1-CN	f (	105 - 118	) KVPQLEIVPNsAEE
4	α S1-CN	f (	105 - 118	) KVPQLEIVPNsAEE
5	α S1-CN	f (	106 - 118	) VPQLEIVPNsAEE
6	α S1-CN	f (	109 - 116	) LEIVPNsA
7	α S1-CN	f (	109 - 117	) LEIVPNsAE
8	α S1-CN	f (	109 - 118	) LEIVPNsAEE
9	α S1-CN	f (	109 - 118	) LEIVPNsAEE
10	α S1-CN	f (	109 - 119	) LEIVPNsAEEER
11	α S1-CN	f (	109 - 119	) LEIVPNsAEEER
12	α S1-CN	f (	110 - 116	) EIVPNsA
13	α S1-CN	f (	110 - 116	) EIVPNsA
14	α S1-CN	f (	110 - 117	) EIVPNsAE
15	α S1-CN	f (	110 - 117	) EIVPNsAE
16	α S1-CN	f (	110 - 118	) EIVPNsAEE
17	α S1-CN	f (	110 - 118	) EIVPNsAEE
18	α S1-CN	f (	110 - 119	) EIVPNsAEEER
19	α S1-CN	f (	110 - 119	) EIVPNsAEEER
20	α S1-CN	f (	111 - 116	) IVPNsA
21	α S1-CN	f (	111 - 119	) IVPNsAEEER
22	α S1-CN	f (	113 - 118	) PNsAEE
23	α S1-CN	f (	113 - 118	) PnsAEE
24	α S1-CN	f (	173 - 186	) YTDAPsFSDIPNPI
25	α S1-CN	f (	174 - 186	) TDAPsFSDIPNPI
26	α S1-CN	f (	180 - 190	) SDIPNPIGsEN
27	α S1-CN	f (	180 - 193	) SDIPNPIGsENSEK
28	α S2-CN	f (	5 - 15	) EHVsssEESII
29	α S2-CN	f (	6 - 15	) HVsssEESII
30	α S2-CN	f (	7 - 13	) VsssEES
31	α S2-CN	f (	7 - 15	) VsssEESII
32	α S2-CN	f (	8&56 - 13&61	) sssEES
33	α S2-CN	f (	8 - 14	) ssSEESI
34	α S2-CN	f (	8 - 14	) sssEESI
35	α S2-CN	f (	9 - 14	) ssEESI
36	α S2-CN	f (	9 - 15	) ssEESII
37	α S2-CN	f (	9 - 16	) ssEESIIIS
38	α S2-CN	f (	9 - 18	) ssEESIIISQE
39	α S2-CN	f (	13 - 18	) SIIsQE
40	α S2-CN	f (	13 - 18	) SIIsqE
41	α S2-CN	f (	13 - 19	) SIIsQET
42	α S2-CN	f (	14 - 19	) IIsQET
43	α S2-CN	f (	25 - 32	) NMAINPsK
44	α S2-CN	f (	25 - 33	) NMAINPsKE
45	α S2-CN	f (	25 - 33	) nMAINPsKE
46	α S2-CN	f (	25 - 33	) NmAINPsKE
47	α S2-CN	f (	25 - 34	) NMAINPsKEN
48	α S2-CN	f (	25 - 35	) NMAINPsKENL
49	α S2-CN	f (	25 - 35	) NmAINPsKENL
50	α S2-CN	f (	26 - 34	) MAINPsKEN
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2	α S2-CN	f (	27 - 32	) AINPsK
3	α S2-CN	f (	27 - 35	) AINPsKENL
4	α S2-CN	f (	27 - 35	) AInPsKENL
5	α S2-CN	f (	29 - 34	) NPsKEN
6	α S2-CN	f (	29 - 35	) NPsKENL
7				
8	α S2-CN	f (	53 - 60	) SIGsssEE
9	α S2-CN	f (	53 - 65	) SIGsssEEsAEVA
10	α S2-CN	f (	61 - 67	) sAEVAtE
11	α S2-CN	f (	61 - 69	) sAEVAtEEV
12	α S2-CN	f (	63 - 69	) EVAtEEV
13	α S2-CN	f (	64 - 69	) VAtEEV
14				
15	α S2-CN	f (	124 - 133	) NREqLStsEE
16	α S2-CN	f (	125 - 133	) REQLsTsEE
17	α S2-CN	f (	126 - 133	) EQLSTsEE
18	α S2-CN	f (	126 - 133	) EQLStsEE
19	α S2-CN	f (	126 - 135	) EQLsTSEENS
20	α S2-CN	f (	126 - 135	) EQLsTsEENS
21	α S2-CN	f (	126 - 136	) EQLsTsEENSK
22	α S2-CN	f (	126 - 136	) EQLsTsEEnSK
23				
24	α S2-CN	f (	128 - 135	) LsTsEENS
25	α S2-CN	f (	137 - 146	) KTVDMEsTEV
26	α S2-CN	f (	138 - 144	) TVDMEsT
27	α S2-CN	f (	138 - 144	) TVDMEST
28	α S2-CN	f (	138 - 145	) TVDMEsTE
29	α S2-CN	f (	138 - 146	) TVDMEsTEV
30	α S2-CN	f (	138 - 146	) TVDmEsTEV
31	α S2-CN	f (	138 - 146	) tVDMEsTEV
32	α S2-CN	f (	139 - 146	) VDMEsTEV
33	α S2-CN	f (	139 - 146	) VDMESTEV
34				
35	α S2-CN	f (	140 - 146	) DMEsTEV
36	α S2-CN	f (	141 - 146	) MEsTEV
37	β -CN	f (	4 - 16	) EELNVPGEIVeSL
38	β -CN	f (	6 - 16	) LNVPGEIVeSL
39	β -CN	f (	7 - 16	) NVPGEIVeSL
40				
41	β -CN	f (	8 - 16	) VPGEIVeSL
42	β -CN	f (	9 - 16	) PGEIVeSL
43	β -CN	f (	10 - 16	) GEIVeSL
44	β -CN	f (	11 - 16	) EIVeSL
45	β -CN	f (	15 - 22	) SLsssEES
46	β -CN	f (	15 - 24	) SLsssEESIT
47				
48	β -CN	f (	16 - 22	) LsssEES
49	β -CN	f (	16 - 23	) LsssEESI
50	β -CN	f (	16 - 24	) LsssEESIT
51				
52	β -CN	f (	17 - 22	) sssEES
53	β -CN	f (	17 - 23	) ssSEESI
54	β -CN	f (	17 - 23	) sssEESI
55	β -CN	f (	17 - 24	) ssSEESIT
56	β -CN	f (	17 - 24	) sssEESIT
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2	β -CN	f (	18 - 23	) ssEESI
3	β -CN	f (	18 - 24	) ssEESIT
4	β -CN	f (	32 - 39	) KFQsEEQQ
5	β -CN	f (	32 - 40	) KFQsEEQQQ
6	β -CN	f (	33 - 38	) FQsEEQ
7	β -CN	f (	33 - 38	) FqsEEQ
8	β -CN	f (	33 - 39	) FQsEEQQ
9	β -CN	f (	33 - 40	) FQsEEQQQ
10	β -CN	f (	33 - 40	) FQsEEQQqQ
11	β -CN	f (	33 - 41	) FQsEEQQQT
12	β -CN	f (	33 - 42	) FQsEEQQQTE
13	β -CN	f (	33 - 42	) FQsEEQQqTE
14	β -CN	f (	33 - 43	) FQsEEQQQTED
15	β -CN	f (	33 - 44	) FQsEEQQQTEDE
16	β -CN	f (	33 - 44	) FQsEEQQqTEDE
17	β -CN	f (	33 - 45	) FQsEEQQQTEDEL
18	β -CN	f (	33 - 45	) FQsEEQQqTEDEL
19	β -CN	f (	33 - 48	) FQsEEQQQTEDELQDK
20	κ -CN A	f (	132 - 140	) STPttEAVE
21	κ -CN	f (	153 - 165	) IESPPEINTVqVt
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leased after digestion according the protocol of Minekus et al. (2014) of Trentingrana cheese at 19 months c
ipitation with CaCl_2 at pH value of:

Modifications	MH+ [Da]	Delta Mass [PPM]	RT [min]	Color code
S7(Phospho)	1026.488	0.93	4.8 n	
N4(Deamidated); S7(Phospho)	1027.471	-0.03	5.0 n	
S5(Phospho)	769.349	-0.09	3.9 b	
N2(Deamidated); S5(Phospho)	770.333	-0.66	4.8 n	
S5(Phospho); S10(Phospho); S12(Phospho)	1990.694	-1.22	8.1 r	
S7(Phospho); S9(Phospho)	1325.492	0.47	6.3 r	
S7(Phospho); S9(Phospho)	1440.518	0.20	6.3 r	
S7(Phospho); S9(Phospho)	1568.575	-0.82	6.1 r	
S6(Phospho); S8(Phospho)	1455.491	-0.91	4.2 r	
S1(Phospho); S6(Phospho); S8(Phospho)	1535.458	-0.56	2.7 r	
S6(Phospho); S8(Phospho)	1657.569	-0.72	7.0 r	
S5(Phospho); S7(Phospho)	1368.459	-0.76	3.3 r	
S5(Phospho); S7(Phospho)	1570.537	-0.65	7.1 r	
S4(Phospho); S6(Phospho)	997.278	-1.86	3.5 r	
S4(Phospho)	1032.340	-0.92	4.9 r	
S4(Phospho); S6(Phospho)	1112.305	-1.64	3.6 r	
S4(Phospho)	1160.400	1.02	5.0 b	
S4(Phospho); S6(Phospho)	1240.363	-1.66	3.5 r	
S4(Phospho); S6(Phospho)	1311.402	-0.52	4.5 r	
S4(Phospho); S6(Phospho); Q10(Deamidated)	1312.386	-0.80	5.9 r	
S4(Phospho); S6(Phospho)	1442.441	-1.21	7.4 r	
S4(Phospho); S6(Phospho); M12(Oxidation)	1702.508	0.25	6.0 r	
S4(Phospho); S6(Phospho)	1927.691	-0.37	11.5 r	
S4(Phospho); S6(Phospho); Q10(Deamidated)	1928.676	0.07	11.8 r	
S4(Phospho); S6(Phospho); M12(Oxidation)	1943.686	-0.26	9.0 r	
S4(Phospho); S6(Phospho); T7(Phospho)	2007.658	-0.24	11.0 r	
S3(Phospho); S5(Phospho)	1125.338	-0.88	2.7 r	
S2(Phospho); S4(Phospho)	1012.252	-2.52	3.5 r	
S6(Phospho)	887.321	-0.57	8.6 r	
S6(Phospho); S8(Phospho); S9(Phospho)	1989.683	-0.21	11.2 r	
S5(Phospho)	759.264	0.84	8.5 b	
S4(Phospho); S6(Phospho); S7(Phospho)	1730.584	-0.41	9.9 r	
S3(Phospho); S4(Phospho); S5(Phospho)	1401.463	0.34	10.3 r	
S2(Phospho); S3(Phospho); S4(Phospho)	1314.430	-0.03	9.4 r	
S1(Phospho); S2(Phospho)	1121.380	-0.42	8.2 r	
S1(Phospho); S2(Phospho); S3(Phospho)	1201.347	0.41	7.9 r	
S1(Phospho); S2(Phospho)	823.252	-0.74	8.0 r	
S1(Phospho)	954.382	0.80	8.5 b	
S1(Phospho); S2(Phospho)	1034.348	-0.29	7.9 r	
S1(Phospho); S2(Phospho); N8(Deamidated)	1035.332	-0.06	8.8 r	

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2	S3(Phospho)	881.376	-0.01	8.9 n
3	S11(Phospho)	1632.789	0.31	13.9 n
4	N10(Deamidated); S11(Phospho)	1633.771	-0.60	14.4 r
5	S10(Phospho)	1504.693	-0.07	14.0 n
6	S7(Phospho)	922.430	2.03	11.8 n
7	N6(Deamidated); S7(Phospho)	1052.454	-0.66	12.3 r
8	S7(Phospho)	1180.514	0.70	11.6 b
9	N6(Deamidated); S7(Phospho)	1181.498	0.49	12.3 b
10	S7(Phospho)	1336.616	1.22	11.0 b
11	N6(Deamidated); S7(Phospho)	1337.597	-1.07	11.5 r
12	S6(Phospho)	809.344	-0.15	8.1 b
13	N5(Deamidated); S6(Phospho)	810.328	0.45	8.7 n
14	S6(Phospho)	938.386	-0.51	7.8 r
15	N5(Deamidated); S6(Phospho)	939.371	-0.20	8.3 r
16	S6(Phospho)	1067.429	0.05	8.1 b
17	N5(Deamidated); S6(Phospho)	1068.414	0.50	8.7 b
18	S6(Phospho)	1223.531	0.11	7.6 b
19	N5(Deamidated); S6(Phospho)	1224.514	-0.20	8.0 b
20	S5(Phospho)	680.302	0.81	5.9 n
21	S5(Phospho)	1094.490	1.68	5.7 b
22	S3(Phospho)	726.234	0.21	11.6 b
23	N2(Deamidated); S3(Phospho)	727.219	0.45	12.3 b
24	S6(Phospho)	1616.688	-0.09	16.9 n
25	S5(Phospho)	1453.626	1.14	16.5 n
26	S9(Phospho)	1222.500	0.73	11.6 n
27	S9(Phospho)	1566.668	-0.01	11.1 n
28	S4(Phospho); S5(Phospho); S6(Phospho)	1456.467	-0.78	10.7 r
29	S3(Phospho); S4(Phospho); S5(Phospho)	1327.425	-0.21	10.7 r
30	S2(Phospho); S3(Phospho); S4(Phospho)	964.198	-0.98	2.1 r
31	S2(Phospho); S3(Phospho); S4(Phospho)	1190.366	-0.22	10.9 r
32	S1(Phospho); S2(Phospho); S3(Phospho)	865.131	0.82	2.0 r
33	S1(Phospho); S2(Phospho)	898.247	-0.98	5.3 r
34	S1(Phospho); S2(Phospho); S3(Phospho)	978.215	0.32	5.7 r
35	S1(Phospho); S2(Phospho)	811.216	-0.43	5.2 r
36	S1(Phospho); S2(Phospho)	924.300	-0.01	10.6 r
37	S1(Phospho); S2(Phospho); S5(Phospho)	1091.298	-0.41	7.6 r
38	S1(Phospho); S2(Phospho); S5(Phospho)	1348.400	0.17	8.5 r
39	S4(Phospho)	756.318	0.34	9.4 b
40	S4(Phospho); Q5(Deamidated)	757.301	-0.64	9.9 r
41	S4(Phospho)	857.366	0.86	10.1 b
42	S3(Phospho)	770.334	1.25	7.1 n
43	S7(Phospho)	954.411	-0.12	7.1 n
44	S7(Phospho)	1083.454	0.17	8.1 n
45	N1(Deamidated); S7(Phospho)	1084.439	0.38	8.3 n
46	M2(Oxidation); S7(Phospho)	1099.450	0.79	5.5 n
47	S7(Phospho)	1197.497	0.28	7.4 n
48	S7(Phospho)	1310.582	0.57	11.4 n
49	M2(Oxidation); S7(Phospho)	1326.578	1.45	9.4 n
50	S6(Phospho)	1083.456	1.40	7.0 n
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S5(Phospho)	709.328	-0.17	2.4 n
S5(Phospho)	1065.499	0.86	8.9 b
N3(Deamidated); S5(Phospho)	1066.484	1.77	9.7 n
S3(Phospho)	768.293	0.18	2.7 n
S3(Phospho)	881.376	-0.01	8.9 n
S4(Phospho); S5(Phospho); S6(Phospho)	1035.235	-0.57	3.3 r
S4(Phospho); S5(Phospho); S6(Phospho)	1492.452	-0.36	7.3 r
S1(Phospho); T6(Phospho)	866.257	-1.50	2.3 r
S1(Phospho); T6(Phospho)	1094.368	-1.07	7.3 r
T4(Phospho)	856.333	-0.78	7.6 r
T3(Phospho)	727.292	0.84	6.5 b
Q4(Deamidated); T7(Phospho); S8(Phospho)	1353.461	0.08	5.7 r
S5(Phospho); S7(Phospho)	1238.433	-0.53	5.0 r
S6(Phospho)	1002.365	-1.67	5.7 r
T5(Phospho); S6(Phospho)	1082.332	-0.95	4.5 r
S4(Phospho)	1203.442	0.82	4.9 n
S4(Phospho); S6(Phospho)	1283.407	-0.68	3.4 r
S4(Phospho); S6(Phospho)	1411.501	-1.48	3.7 r
S4(Phospho); S6(Phospho); N9(Deamidated)	1412.486	-0.79	3.2 r
S2(Phospho); S4(Phospho)	1026.306	-0.39	2.4 r
S7(Phospho)	1218.496	-0.30	9.2 b
S6(Phospho)	862.290	0.15	6.0 r
T7(Phospho)	862.291	1.35	6.0 n
S6(Phospho)	991.333	0.32	5.7 r
S6(Phospho)	1090.400	-0.61	9.6 b
M4(Oxidation); S6(Phospho)	1106.397	1.28	6.5 b
T1(Phospho); S6(Phospho)	1170.367	-0.27	9.0 r
S5(Phospho)	989.353	-0.47	9.4 r
T6(Phospho)	989.354	0.52	9.4 n
S4(Phospho)	890.285	0.43	7.8 b
S3(Phospho)	775.258	0.15	6.4 b
S12(Phospho)	1507.693	-0.02	16.5 b
S10(Phospho)	1249.608	0.07	16.2 b
S9(Phospho)	1136.524	0.16	14.1 b
S8(Phospho)	1022.480	-0.75	13.6 r
S7(Phospho)	923.413	0.36	14.1 b
S6(Phospho)	826.359	-0.07	12.2 r
S5(Phospho)	769.339	0.86	11.7 b
S3(Phospho); S4(Phospho); S5(Phospho)	1065.247	0.54	2.5 r
S3(Phospho); S4(Phospho); S5(Phospho)	1279.379	0.42	7.9 r
S2(Phospho); S3(Phospho); S4(Phospho)	978.214	-0.55	1.9 r
S2(Phospho); S3(Phospho); S4(Phospho)	1091.298	-0.41	7.6 r
S2(Phospho); S3(Phospho); S4(Phospho)	1192.346	-0.02	7.0 r
S1(Phospho); S2(Phospho); S3(Phospho)	865.131	0.82	2.0 r
S1(Phospho); S2(Phospho)	898.247	-0.98	5.3 r
S1(Phospho); S2(Phospho); S3(Phospho)	978.215	0.32	5.7 r
S1(Phospho); S2(Phospho)	999.295	-0.77	5.0 r
S1(Phospho); S2(Phospho); S3(Phospho)	1079.261	-0.51	6.1 r

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2	S1(Phospho); S2(Phospho)	811.216	-0.43	5.2 r
3	S1(Phospho); S2(Phospho)	912.263	-0.66	4.6 r
4	S4(Phospho)	1103.443	1.94	3.6 n
5	S4(Phospho)	1231.499	0.07	3.7 n
6	S3(Phospho)	847.287	0.22	2.7 b
7	Q2(Deamidated); S3(Phospho)	848.270	-1.01	3.9 r
8	S3(Phospho)	975.345	-0.92	3.1 b
9	S3(Phospho)	1103.404	-0.15	3.1 b
10	S3(Phospho); Q7(Deamidated)	1104.387	-0.71	3.7 n
11	S3(Phospho)	1204.451	-0.40	4.2 r
12	S3(Phospho)	1333.494	-0.08	4.7 r
13	S3(Phospho); Q8(Deamidated)	1334.480	0.83	5.3 r
14	S3(Phospho)	1448.521	-0.40	4.8 r
15	S3(Phospho)	1577.564	-0.08	5.6 r
16	S3(Phospho); Q8(Deamidated)	1578.547	-0.83	6.1 r
17	S3(Phospho)	1690.650	0.91	10.1 b
18	S3(Phospho); Q8(Deamidated)	1691.633	0.40	10.4 n
19	S3(Phospho)	2061.829	0.41	8.5 b
20	T4(Phospho); T5(Phospho)	1094.368	-0.95	7.3 r
21	Q11(Deamidated); T13(Phospho)	1507.691	-0.90	16.5 r
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36	3	0	3
37	2	0	2
38	3	0	3
39	2	0	2
40	2	0	2
41	3	0	3
42	3	0	3
43	1	0	1
44	1	0	1
45	1	0	1
46	1	0	1
47	1	0	1
48	1	0	1
49	1	0	1
50	1	0	1
51	1	0	1
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54	1	0	1
55	1	0	1
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57	1	0	1
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2	1	0	1
3	1	0	1
4	1	0	1
5	1	0	1
6	1	0	1
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8	3	0	3
9	3	0	3
10	1	1	2
11	1	1	2
12	0	1	1
13	0	1	1
14	1	1	2
15	2	0	2
16	1	0	1
17	1	1	2
18	1	0	1
19	2	0	2
20	2	0	2
21	2	0	2
22	2	0	2
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24	2	0	2
25	1	0	1
26	1	0	1
27	0	1	1
28	1	0	1
29	1	0	1
30	1	0	1
31	1	1	2
32	1	0	1
33	0	1	1
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35	1	0	1
36	1	0	1
37	1	0	1
38	1	0	1
39	1	0	1
40	1	0	1
41	1	0	1
42	1	0	1
43	1	0	1
44	1	0	1
45	3	0	3
46	3	0	3
47	3	0	3
48	3	0	3
49	3	0	3
50	3	0	3
51	3	0	3
52	2	0	2
53	3	0	3
54	2	0	2
55	3	0	3
56	2	0	2
57	3	0	3
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2	2	0	2
3	2	0	2
4	1	0	1
5	1	0	1
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11	1	0	1
12	1	0	1
13	1	0	1
14	1	0	1
15	1	0	1
16	1	0	1
17	1	0	1
18	1	0	1
19	1	0	1
20	1	0	1
21	1	0	1
22	0	2	2
23	0	1	1
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Peptide length	Max peptide length	Min peptide length
8	16	6
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26	11
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29	14
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31	10
32	7
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37	7
38	6
39	7
40	8
41	10
42	6
43	6
44	7
45	8
46	10
47	6
48	6
49	8
50	9
51	9
52	9
53	10
54	11
55	11
56	9
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For Peer Review

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18	10
19	10
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23	10
24	7
25	7
26	8
27	9
28	9
29	9
30	8
31	8
32	8
33	7
34	6
35	13
36	11
37	10
38	9
39	8
40	7
41	6
42	8
43	10
44	7
45	8
46	9
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For Peer Review

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For Peer Review

Supplementary Table S2. TN_26_COST. Caseinophosphopeptides re
CPPs isolated from cheese digesta by selective pre
pH 8.0 are indicated in black;
pH 4.6 are indicated in red;
both, pH 8.0 and pH 4.6, are indicated in blue.

Protein fragment	Sequence
α S1-CN f (35 - 42)	EKVNELsK
α S1-CN f (35 - 42)	EKVnELsK
α S1-CN f (37 - 42)	VNELsK
α S1-CN f (37 - 52)	VNELsKDIGsEsTEDQ
α S1-CN f (39 - 52)	ELSKDIGSEstEDQ
α S1-CN f (40 - 50)	LSKDIGsEsTE
α S1-CN f (40 - 51)	LSKDIGsEsTED
α S1-CN f (40 - 52)	LSKDIGsEsTEDQ
α S1-CN f (40 - 54)	LSKDIGSEstEDQAM
α S1-CN f (41 - 52)	SKDIGsEsTEDQ
α S1-CN f (41 - 53)	SKDIGsEsTEDQA
α S1-CN f (41 - 52)	sKDIGsEsTEDQ
α S1-CN f (41 - 54)	SKDIGsEsTEDQAM
α S1-CN f (41 - 54)	sKDIGsEsTEDQAM
α S1-CN f (42 - 52)	KDIGsEsTEDQ
α S1-CN f (42 - 54)	KDIGsEsTEDQAM
α S1-CN f (43 - 50)	DIGsEsTE
α S1-CN f (43 - 51)	DIGsEsTED
α S1-CN f (43 - 52)	DIGsESTEDQ
α S1-CN f (43 - 52)	DIGsEsTEDQ
α S1-CN f (43 - 53)	DIGsEsTEDQA
α S1-CN f (43 - 53)	DIGsEsTEDqA
α S1-CN f (43 - 54)	DIGSEstEDQAM
α S1-CN f (43 - 54)	DIGsEsTEDQAM
α S1-CN f (43 - 55)	DIGsEsTEDQAME
α S1-CN f (43 - 57)	DIGsEsTEDQAmEDI
α S1-CN f (43 - 58)	DIGSEstEDQAMEDIK
α S1-CN f (43 - 58)	DIGsEsTEDqAMEDIK
α S1-CN f (43 - 58)	DIGsEsTEDQAmEDIK
α S1-CN f (43 - 58)	DIGsEstEDQAMEDIK
α S1-CN f (44 - 52)	IGsEsTEDQ
α S1-CN f (45 - 52)	GsEsTEDQ
α S1-CN f (59 - 65)	QMEAEsl
α S1-CN f (59 - 74)	QMEAEslssSEEIVPN
α S1-CN f (60 - 65)	MEAEsl
α S1-CN f (61 - 74)	EAEslssSEEIVPN
α S1-CN f (64 - 74)	SIssEEIVPN
α S1-CN f (65 - 74)	ISssEEIVPN
α S1-CN f (65 - 74)	ISSsEEIVPN
α S1-CN f (66 - 74)	ssSEEIVPN

1				
2	α S1-CN	f (	66 - 74	) sssEEIVPN
3	α S1-CN	f (	67 - 72	) ssEEIV
4	α S1-CN	f (	67 - 74	) SsEEIVPN
5	α S1-CN	f (	67 - 74	) sSEEIVPN
6	α S1-CN	f (	67 - 74	) ssEEIVPN
7	α S1-CN	f (	67 - 74	) ssEEIVPn
8	α S1-CN	f (	67 - 78	) ssEEIVPNsVEQ
9	α S1-CN	f (	67 - 79	) ssEEIVPNsVEQK
10	α S1-CN	f (	70 - 78	) EIVPNsVEQ
11	α S1-CN	f (	105 - 118	) KVPQLEIVPNsAEE
12	α S1-CN	f (	105 - 118	) KVPQLEIVPNsAEE
13	α S1-CN	f (	106 - 118	) VPQLEIVPNsAEE
14	α S1-CN	f (	106 - 119	) VPQLEIVPNsAEER
15	α S1-CN	f (	106 - 119	) VPQLEIVPNsAEER
16	α S1-CN	f (	109 - 118	) LEIVPNsAEE
17	α S1-CN	f (	109 - 118	) LEIVPNsAEE
18	α S1-CN	f (	109 - 119	) LEIVPNsAEER
19	α S1-CN	f (	109 - 119	) LEIVPNsAEER
20	α S1-CN	f (	110 - 116	) EIVPNsA
21	α S1-CN	f (	110 - 116	) EIVPNsA
22	α S1-CN	f (	110 - 117	) EIVPNsAE
23	α S1-CN	f (	110 - 117	) EIVPNsAE
24	α S1-CN	f (	110 - 118	) EIVPNsAEE
25	α S1-CN	f (	110 - 118	) EIVPNsAEE
26	α S1-CN	f (	110 - 119	) EIVPNsAEER
27	α S1-CN	f (	110 - 119	) EIVPNsAEER
28	α S1-CN	f (	111 - 119	) IVPNsAEER
29	α S1-CN	f (	112 - 119	) VPNsAEER
30	α S1-CN	f (	113 - 118	) PNsAEE
31	α S1-CN	f (	113 - 118	) PnsAEE
32	α S1-CN	f (	173 - 186	) YTDAPsFSDIPNPI
33	α S1-CN	f (	174 - 186	) TDAPsFSDIPNPI
34	α S1-CN	f (	180 - 190	) SDIPNPIGsEN
35	α S1-CN	f (	180 - 193	) SDIPNPIGsENSEK
36	α S2-CN	f (	5 - 15	) EHVsssEESII
37	α S2-CN	f (	6 - 15	) HVsssEESII
38	α S2-CN	f (	7 - 13	) VsssEES
39	α S2-CN	f (	7 - 15	) VsssEESII
40	α S2-CN	f (	7 - 16	) VsssEESIIS
41	α S2-CN	f (	8 - 14	) ssSEESI
42	α S2-CN	f (	9 - 14	) ssEESI
43	α S2-CN	f (	9 - 15	) ssEESII
44	α S2-CN	f (	9 - 16	) ssEESIIS
45	α S2-CN	f (	9 - 16	) ssEESIIS
46	α S2-CN	f (	13 - 18	) SIIsQE
47	α S2-CN	f (	13 - 19	) SIIsQET
48	α S2-CN	f (	25 - 32	) NMAINPsK
49	α S2-CN	f (	25 - 33	) NMAINPsKE
50	α S2-CN	f (	25 - 33	) NMAInPsKE
51				
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2	α S2-CN	f (	25 - 33	) NmAInPsKE
3	α S2-CN	f (	25 - 34	) NMAInPsKEN
4	α S2-CN	f (	25 - 35	) NmAInPsKENL
5	α S2-CN	f (	26 - 35	) MAInPsKENL
6	α S2-CN	f (	27 - 32	) AInPsK
7	α S2-CN	f (	27 - 32	) AInPsK
8	α S2-CN	f (	27 - 35	) AInPsKENL
9	α S2-CN	f (	27 - 35	) AInPsKENL
10	α S2-CN	f (	29 - 35	) NPsKENL
11	α S2-CN	f (	53 - 60	) SIGsssEE
12	α S2-CN	f (	53 - 65	) SIGSsSEsAEVA
13	α S2-CN	f (	61 - 69	) sAEVAtEEV
14	α S2-CN	f (	64 - 69	) VAtEEV
15	α S2-CN	f (	124 - 133	) NREQLSsEE
16	α S2-CN	f (	124 - 133	) NREQLSsEE
17	α S2-CN	f (	125 - 133	) REQLSsEE
18	α S2-CN	f (	126 - 133	) EQLSsEE
19	α S2-CN	f (	126 - 133	) EQLSsEE
20	α S2-CN	f (	126 - 133	) EQLSsEE
21	α S2-CN	f (	126 - 135	) EQLsTsEENS
22	α S2-CN	f (	126 - 136	) EQLsTsEENSK
23	α S2-CN	f (	126 - 136	) EQLsTsEENSK
24	α S2-CN	f (	126 - 136	) EQLsTsEENSK
25	α S2-CN	f (	137 - 146	) KTVDMEsTEV
26	α S2-CN	f (	137 - 146	) KTVDMEsTEV
27	α S2-CN	f (	138 - 144	) TVDMEsT
28	α S2-CN	f (	138 - 144	) TVDMEsT
29	α S2-CN	f (	138 - 145	) TVDMEsTE
30	α S2-CN	f (	138 - 145	) TVDMEsTE
31	α S2-CN	f (	138 - 145	) TVDMEsTE
32	α S2-CN	f (	138 - 146	) TVDMEsTEV
33	α S2-CN	f (	138 - 146	) TVDMEsTEV
34	α S2-CN	f (	138 - 146	) TVDMEsTEV
35	α S2-CN	f (	138 - 146	) TVDMEsTEV
36	α S2-CN	f (	139 - 146	) VDMEsTEV
37	α S2-CN	f (	140 - 146	) DMEsTEV
38	α S2-CN	f (	141 - 146	) MEsTEV
39	β -CN	f (	4 - 16	) EELNVPGEIVeSL
40	β -CN	f (	6 - 16	) LNVPGEIVeSL
41	β -CN	f (	7 - 16	) NVPGEIVeSL
42	β -CN	f (	8 - 16	) VPGEIVeSL
43	β -CN	f (	9 - 16	) PGEIVeSL
44	β -CN	f (	10 - 16	) GEIVeSL
45	β -CN	f (	11 - 16	) EIVeSL
46	β -CN	f (	15 - 22	) SLsssEES
47	β -CN	f (	15 - 24	) SLsssEESIT
48	β -CN	f (	16 - 22	) LsssEES
49	β -CN	f (	16 - 23	) LsssEESi
50	β -CN	f (	16 - 24	) LsssEESIT
51	β -CN	f (	17 - 23	) ssSEESI
52	β -CN	f (	17 - 24	) ssSEESIT
53	β -CN	f (	17 - 24	) sssEESIT
54	β -CN	f (	18 - 23	) ssEESI
55	β -CN	f (	18 - 23	) ssEESI
56	β -CN	f (	18 - 23	) ssEESI
57	β -CN	f (	18 - 23	) ssEESI
58	β -CN	f (	18 - 23	) ssEESI
59	β -CN	f (	18 - 23	) ssEESI
60	β -CN	f (	18 - 23	) ssEESI

1				
2	β -CN	f (	18 - 24	) ssEESIT
3	β -CN	f (	32 - 39	) KFQsEEQQ
4	β -CN	f (	32 - 40	) KFQsEEQQQ
5	β -CN	f (	32 - 44	) KFQsEEQQQTEDE
6	β -CN	f (	33 - 38	) FQsEEQ
7	β -CN	f (	33 - 39	) FQsEEQQ
8	β -CN	f (	33 - 40	) FQsEEQQQ
9	β -CN	f (	33 - 40	) FQsEEQqQ
10	β -CN	f (	33 - 42	) FQsEEQQQTE
11	β -CN	f (	33 - 43	) FQsEEQQQTED
12	β -CN	f (	33 - 44	) FQsEEQQQTEDE
13	β -CN	f (	33 - 44	) FQsEEqQQTEDE
14	β -CN	f (	33 - 45	) FQsEEQQQTEDEL
15	β -CN	f (	33 - 45	) FQsEEQqQTEDEL
16	β -CN	f (	33 - 48	) FQsEEQQQTEDELQDK
17	β -CN	f (	33 - 48	) FQsEEQqQTEDELQDK
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released after digestion according the protocol of Minekus et al. (2014) of Trentingrana cheese at 26 months
 precipitation with CaCl_2 at pH value of:

Modifications	MH+ [Da]	Delta Mass [PPM]	RT [min]
S7(Phospho)	1026.487	-0.02	4.8
N4(Deamidated); S7(Phospho)	1027.469	-1.57	4.9
S5(Phospho)	769.349	-0.73	3.8
S5(Phospho); S10(Phospho); S12(Phospho)	1990.695	-0.67	8.2
S10(Phospho); T11(Phospho)	1697.619	-0.33	6.9
S7(Phospho); S9(Phospho)	1325.490	-1.00	6.2
S7(Phospho); S9(Phospho)	1440.519	0.62	6.3
S7(Phospho); S9(Phospho)	1568.576	-0.36	6.2
S9(Phospho); T10(Phospho)	1770.654	-0.17	8.5
S6(Phospho); S8(Phospho)	1455.492	-0.58	4.3
S6(Phospho); S8(Phospho)	1526.530	0.00	5.7
S1(Phospho); S6(Phospho); S8(Phospho)	1535.457	-1.36	3.1
S6(Phospho); S8(Phospho)	1657.569	-0.79	7.4
S1(Phospho); S6(Phospho); S8(Phospho)	1737.536	0.01	6.6
S5(Phospho); S7(Phospho)	1368.460	-0.67	3.2
S5(Phospho); S7(Phospho)	1570.537	-0.73	7.1
S4(Phospho); S6(Phospho)	997.279	-1.25	3.6
S4(Phospho); S6(Phospho)	1112.306	-0.66	3.6
S4(Phospho)	1160.398	-1.23	5.0
S4(Phospho); S6(Phospho)	1240.365	-0.28	4.3
S4(Phospho); S6(Phospho)	1311.403	0.60	5.8
S4(Phospho); S6(Phospho); Q10(Deamidated)	1312.387	0.31	5.9
S6(Phospho)	1362.477	0.34	7.7
S4(Phospho); S6(Phospho)	1442.442	-0.71	7.4
S4(Phospho); S6(Phospho)	1571.485	-0.26	7.2
S4(Phospho); S6(Phospho); M12(Oxidation)	1815.591	-0.28	10.1
S6(Phospho); T7(Phospho)	1927.691	-0.56	10.1
S4(Phospho); S6(Phospho); Q10(Deamidated)	1928.675	-0.24	11.8
S4(Phospho); S6(Phospho); M12(Oxidation)	1943.687	0.05	9.0
S4(Phospho); S6(Phospho); T7(Phospho)	2007.659	0.37	11.0
S3(Phospho); S5(Phospho)	1125.338	-0.08	2.6
S2(Phospho); S4(Phospho)	1012.253	-1.56	3.6
S6(Phospho)	887.322	0.05	8.6
S6(Phospho); S8(Phospho); S9(Phospho)	1989.684	-0.15	11.8
S5(Phospho)	759.263	-0.52	8.5
S4(Phospho); S6(Phospho); S7(Phospho)	1730.584	-0.34	10.0
S3(Phospho); S4(Phospho); S5(Phospho)	1401.463	0.51	10.0
S3(Phospho); S4(Phospho)	1234.464	0.15	9.5
S2(Phospho); S3(Phospho); S4(Phospho)	1314.430	-0.03	9.1
S1(Phospho); S2(Phospho)	1121.379	-0.53	8.2

1				
2	S1(Phospho); S2(Phospho); S3(Phospho)	1201.346	-0.31	8.0
3	S1(Phospho); S2(Phospho)	823.251	-0.96	8.0
4	S2(Phospho)	954.381	-0.61	8.5
5	S1(Phospho)	954.382	0.16	8.5
6	S1(Phospho); S2(Phospho)	1034.348	-0.29	7.9
7	S1(Phospho); S2(Phospho); N8(Deamidated)	1035.332	-0.29	8.7
8	S1(Phospho); S2(Phospho); S9(Phospho)	1557.515	-0.31	8.9
9	S1(Phospho); S2(Phospho); N8(Deamidated); S9(Phospho)	1686.593	-1.31	8.3
10	S6(Phospho)	1094.476	-0.47	9.1
11	S11(Phospho)	1632.787	-0.74	13.9
12	N10(Deamidated); S11(Phospho)	1633.771	-0.60	14.4
13	S10(Phospho)	1504.692	-0.56	14.0
14	S10(Phospho)	1660.793	-0.76	13.5
15	N9(Deamidated); S10(Phospho)	1661.778	-0.10	13.8
16	S7(Phospho)	1180.512	-0.79	11.6
17	N6(Deamidated); S7(Phospho)	1181.497	-0.03	12.3
18	S7(Phospho)	1336.614	-0.24	11.0
19	N6(Deamidated); S7(Phospho)	1337.598	-0.43	11.5
20	S6(Phospho)	809.343	-1.05	8.1
21	N5(Deamidated); S6(Phospho)	810.327	-0.83	8.7
22	S6(Phospho)	938.387	-0.19	7.8
23	N5(Deamidated); S6(Phospho)	939.370	-0.59	8.4
24	S6(Phospho)	1067.429	-0.63	8.1
25	N5(Deamidated); S6(Phospho)	1068.413	-0.41	8.7
26	S6(Phospho)	1223.529	-1.19	7.7
27	N5(Deamidated); S6(Phospho)	1224.513	-0.89	8.2
28	S5(Phospho)	1094.488	-0.22	5.6
29	S4(Phospho)	981.403	-1.26	7.6
30	S3(Phospho)	726.234	-0.88	11.6
31	N2(Deamidated); S3(Phospho)	727.218	-0.56	12.3
32	S6(Phospho)	1616.687	-0.54	16.9
33	S5(Phospho)	1453.624	-0.79	16.5
34	S9(Phospho)	1222.498	-1.01	11.6
35	S9(Phospho)	1566.668	-0.47	11.0
36	S4(Phospho); S5(Phospho); S6(Phospho)	1456.468	-0.36	10.7
37	S3(Phospho); S4(Phospho); S5(Phospho)	1327.426	0.25	10.7
38	S2(Phospho); S3(Phospho); S4(Phospho)	964.198	-0.66	2.0
39	S2(Phospho); S3(Phospho); S4(Phospho)	1190.367	0.40	11.0
40	S2(Phospho); S3(Phospho); S4(Phospho)	1277.400	1.10	9.4
41	S1(Phospho); S2(Phospho)	898.248	0.04	5.3
42	S1(Phospho); S2(Phospho)	811.216	-0.13	5.1
43	S1(Phospho); S2(Phospho)	924.300	-0.21	10.6
44	S1(Phospho); S2(Phospho)	1011.332	-0.17	8.8
45	S1(Phospho); S2(Phospho); S5(Phospho)	1091.298	0.15	7.7
46	S4(Phospho)	756.318	0.02	9.4
47	S4(Phospho)	857.366	0.57	10.1
48	S7(Phospho)	954.411	-0.63	7.1
49	S7(Phospho)	1083.453	-0.96	8.1
50	N5(Deamidated); S7(Phospho)	1084.438	-0.29	9.1
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2	M2(Oxidation); S7(Phospho)	1099.449	0.35	5.5
3	S7(Phospho)	1197.496	-0.53	7.4
4	M2(Oxidation); S7(Phospho)	1326.577	0.53	9.4
5	S6(Phospho)	1196.539	0.28	11.2
6	S5(Phospho)	709.327	-1.12	2.4
7	S5(Phospho)	1065.498	-0.05	8.9
8	N3(Deamidated); S5(Phospho)	1066.483	1.09	9.7
9	S3(Phospho)	881.376	-0.70	8.9
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11	S4(Phospho); S5(Phospho); S6(Phospho)	1035.235	-0.68	3.0
12	S5(Phospho); S6(Phospho); S9(Phospho)	1492.452	-0.36	7.1
13	S1(Phospho); T6(Phospho)	1094.368	-0.74	7.3
14	T3(Phospho)	727.291	0.09	6.5
15	S6(Phospho); S8(Phospho)	1352.477	0.08	5.2
16	Q4(Deamidated); T7(Phospho); S8(Phospho)	1353.461	0.08	5.7
17	S5(Phospho); S7(Phospho)	1238.434	0.16	5.1
18	S6(Phospho)	1002.365	-1.00	5.7
19	T5(Phospho); S6(Phospho)	1082.332	-0.61	4.4
20	S4(Phospho); S6(Phospho)	1283.407	-0.58	3.2
21	S4(Phospho); S6(Phospho)	1411.502	-0.53	3.8
22	S4(Phospho); S6(Phospho); N9(Deamidated)	1412.487	-0.01	3.4
23	T8(Phospho)	1218.495	-0.90	9.2
24	S7(Phospho)	1218.496	-0.10	9.2
25	S6(Phospho)	862.289	-1.41	6.1
26	T7(Phospho)	862.291	0.57	6.0
27	T7(Phospho)	991.333	0.56	6.3
28	S6(Phospho)	991.333	0.81	6.3
29	T7(Phospho)	1090.399	-1.61	9.6
30	M4(Oxidation); S6(Phospho)	1106.396	-0.42	6.6
31	M4(Oxidation); T7(Phospho)	1106.396	-0.08	6.6
32	T1(Phospho); S6(Phospho)	1170.367	-0.27	9.0
33	T6(Phospho)	989.354	0.27	9.4
34	S4(Phospho)	890.284	-1.48	9.6
35	S3(Phospho)	775.258	-0.48	6.4
36	S12(Phospho)	1507.692	-0.58	16.5
37	S10(Phospho)	1249.607	-0.42	16.2
38	S9(Phospho)	1136.523	-0.60	14.1
39	S8(Phospho)	1022.480	-0.45	13.6
40	S7(Phospho)	923.411	-1.29	14.1
41	S6(Phospho)	826.359	-0.81	12.2
42	S5(Phospho)	769.337	-0.73	11.7
43	S3(Phospho); S4(Phospho); S5(Phospho)	1065.248	1.45	2.5
44	S3(Phospho); S4(Phospho); S5(Phospho)	1279.378	-0.25	8.0
45	S2(Phospho); S3(Phospho); S4(Phospho)	978.215	0.51	1.9
46	S2(Phospho); S3(Phospho); S4(Phospho)	1091.298	-0.18	7.5
47	S2(Phospho); S3(Phospho); S4(Phospho)	1192.346	0.12	7.2
48	S1(Phospho); S2(Phospho)	898.248	0.04	5.3
49	S1(Phospho); S2(Phospho)	999.295	-0.59	4.8
50	S1(Phospho); S2(Phospho); S3(Phospho)	1079.262	0.39	6.5
51	S1(Phospho); S2(Phospho)	811.216	-0.13	5.1
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2	S1(Phospho); S2(Phospho)	912.263	-0.26	4.6
3	S4(Phospho)	1103.440	-0.49	3.6
4	S4(Phospho)	1231.499	-0.33	3.8
5	S4(Phospho)	1705.659	0.10	6.0
6	S3(Phospho)	847.286	-1.58	3.2
7	S3(Phospho)	975.344	-1.36	2.9
8	S3(Phospho)	1103.403	-1.14	3.2
9	S3(Phospho); Q7(Deamidated)	1104.387	-0.82	3.7
10	S3(Phospho)	1333.495	0.10	4.8
11	S3(Phospho)	1448.521	-0.56	4.9
12	S3(Phospho)	1577.564	-0.13	5.6
13	S3(Phospho); Q6(Deamidated)	1578.549	0.41	6.0
14	S3(Phospho)	1690.648	-0.17	10.1
15	S3(Phospho); Q8(Deamidated)	1691.632	-0.18	10.5
16	S3(Phospho)	2061.828	-0.06	8.4
17	S3(Phospho); Q8(Deamidated)	2062.813	0.35	9.5
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s of ripening

Color code	Number of phosphorylated serine residues per peptide	Number of phosphorylated threonine residues per peptide
n	1	0
n	1	0
b	1	0
r	3	0
r	1	1
r	2	0
r	2	0
r	2	0
r	1	1
r	2	0
r	2	0
r	3	0
r	2	0
r	3	0
r	2	0
r	2	0
r	2	0
r	2	0
b	1	0
r	2	0
r	2	0
r	2	0
b	1	0
r	2	0
r	2	0
r	2	0
r	2	1
r	2	0
r	2	0
r	2	0
r	1	0
r	3	0
b	1	0
r	3	0
r	3	0
r	2	0
r	3	0
r	2	0

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2	r	3	0
3	r	2	0
4	n	1	0
5	r	1	0
6	r	2	0
7	r	2	0
8	r	3	0
9	r	3	0
10	n	1	0
11	b	1	0
12	r	1	0
13	n	1	0
14	n	1	0
15	n	1	0
16	b	1	0
17	b	1	0
18	b	1	0
19	b	1	0
20	b	1	0
21	b	1	0
22	n	1	0
23	n	1	0
24	r	1	0
25	b	1	0
26	b	1	0
27	b	1	0
28	b	1	0
29	b	1	0
30	b	1	0
31	b	1	0
32	n	1	0
33	b	1	0
34	b	1	0
35	n	1	0
36	n	1	0
37	n	1	0
38	n	1	0
39	n	1	0
40	r	3	0
41	r	3	0
42	r	3	0
43	r	3	0
44	r	3	0
45	r	3	0
46	r	2	0
47	r	2	0
48	r	2	0
49	r	2	0
50	r	2	0
51	r	3	0
52	b	1	0
53	b	1	0
54	n	1	0
55	n	1	0
56	n	1	0
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For Peer Review

1			
2	n	1	0
3	n	1	0
4	n	1	0
5	n	1	0
6	n	1	0
7			
8	b	1	0
9	n	1	0
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11	r	3	0
12	r	3	0
13	r	1	1
14	b	0	1
15	r	2	0
16	r	1	1
17	r	2	0
18	r	1	0
19	r	1	1
20	r	2	0
21	r	2	0
22	r	2	0
23	r	2	0
24	n	0	1
25	r	1	0
26	n	1	0
27	r	0	1
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29	n	1	0
30	b	0	1
31	n	1	0
32	r	0	1
33	r	1	1
34	b	0	1
35	b	1	0
36	b	1	0
37	b	1	0
38	b	1	0
39	b	1	0
40	b	1	0
41	b	1	0
42	r	1	0
43	b	1	0
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45	r	1	0
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52	r	3	0
53	r	2	0
54	r	2	0
55	r	3	0
56	r	2	0
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1			
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3	n	1	0
4	n	1	0
5	r	1	0
6	b	1	0
7	b	1	0
8	b	1	0
9	n	1	0
10	r	1	0
11	r	1	0
12	r	1	0
13	r	1	0
14	r	1	0
15	b	1	0
16	n	1	0
17	b	1	0
18	r	1	0
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For Peer Review

Number of phosphorylated residues per peptides	Peptide length	Max peptide length	Min peptide length
1	8	16	6
1	8		
1	6		
3	16		
2	14		
2	11		
2	12		
2	13		
2	15		
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2	13		
2	15		
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3	16		
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3	10		
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2	3	9
3	2	6
4	1	8
5	1	8
6	2	8
7	2	8
8	3	12
9	3	13
10	1	9
11	1	14
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36	3	11
37	3	10
38	3	7
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45	3	8
46	1	6
47	1	7
48	1	8
49	1	9
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13	2	9
14	1	6
15	2	10
16	2	10
17	2	9
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49	3	10
50	3	7
51	3	8
52	3	9
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56	2	6
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