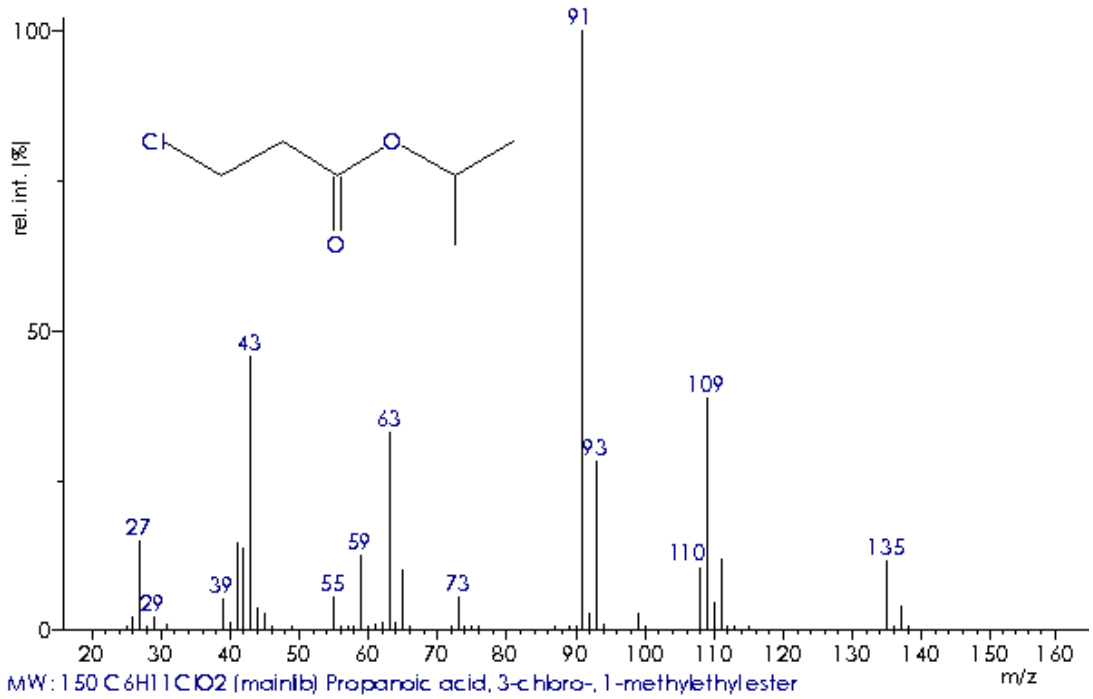
Answer 6.12

Identify the unknown from its 70 eV EI mass spectrum. According to a FI mass spectrum acquired in addition, the peak at *m/z* 135 has been identified as $[M\text{-}CH_3]^+$.



Due to the FI mass spectrum, $M^{+\bullet}$ = 150. In the EI mass spectrum $M^{+\bullet}$ is absent, i.e., the molecular ion readily undergoes fragmentation.
The even mass indicates 0, 2, 4, ... nitrogen atoms.
The isotopic pattern of $[M\text{-}CH_3]^+$ results from Cl (and carbon of course).

m/z 135, 137	[M–15], Cl pattern, $[M–CH_3]^+$
m/z 109, 111	[M–41], Cl pattern, $[M–C_3H_5]^+$?
m/z 108, 110	[M–42], Cl pattern, $[M–C_3H_6]^+$?
m/z 91, 93 (base peak)	[M–59], Cl pattern, $[M–COOMe]^+$ or $[M–OPr]^+$?
m/z 73	[M–77] ?
m/z 63, 65	Cl pattern
m/z 59	$[COOMe]^+$ or $[OPr]^+$?
m/z 43	most probably propyl ion (accompanied by *m/z* 39, 41)

Observations:
i) one series of reactions keeps the chlorine in the ion, the other series (of minor intensity) eliminates the chlorine, too;

ii) the unstable molecular ion eliminates $C_3H_5^{\bullet}$ *and* C_3H_6 indicating the dominant occurrence of McL with double hydrogen transfer plus „normal“ McL.

The assignment of a structure has to start with two assumptions: it could be an ester with a secondary alcohol → isopropyl according to $C_3H_5^{\bullet}$ and C_3H_6 loss. The chlorine is in the carboxylic acid side of the molecule.

Subtracting 35 u (Cl) and 44 u (COO for ester) from 150 u leaves 71 u which fits to 5×14 u + 1u, i.e., C_5H_{11} in total, C_3H_7 of which belong to the former alcohol. Therefore, only C_2H_4 is left.

The empirical formula is $C_6H_{11}ClO_2$; r+d = $6 - 0.5 \times (11 + 1) + 1 = 1$

The fragmentation scheme verifies the structure: