

experimental errors. That the activity coefficient variation should cause this spread we find less probable.

Separate studies of the range $Z_n < 4$ (assuming $n = 1, 2, 3$, and 4) and determinations of $K_a(\text{C}_3\text{H}_5\text{N}_2^+)$ gave the equilibrium constants and standard deviations collected in Table 1. In these separate investigations the upper limits for the concentration ranges (in mM) were: 3 M (Na)ClO₄, (3 M (Na)Cl); $B = 20$, (80); $C = 330$, (324) [$\text{C}_3\text{H}_4\text{N}_2$] = 281, (111).

Within these concentration ranges, the acidity constant of $\text{C}_3\text{H}_5\text{N}_2^+$ appeared to be independent of C , and the formation constants for the different copper complexes were independent of B and C as long as $C/B \geq 8$. This supports our assumption that activity factors cannot cause the spread at $Z_n > 5$.

Calculations and results. First we will try to explain the range $3 \leq Z_n \leq 5$, where the different Z_n -curves seem to coincide (cf. Figs. 1a and 1b). The results of the calculations of main interest are given in Table 2. A rather good fit to experimental data is obtained in 3 M (Na)ClO₄ as well as in 3 M (Na)Cl, if one introduces the formation constants β_5 and β_6 to the model with only four mononuclear complexes $\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_n^{2+}$, ($n = 1 \dots 4$). In 3 M (Na)Cl this model fits data better than a correction in C , ΔC and K_a without β_5 and β_6 . In 3 M (Na)ClO₄ a good fit is obtained with a variation in C without β_5 and β_6 . However, ΔC appears too great to be experimentally possible (in some instances 4–9 %). A somewhat better fit is obtained if, in addition to a correction in C , β_5 and β_6 were introduced. In this case the corrections in C become more tolerable (cf. Table 2).

We consider next the data range extended to include data where $Z_n > 5$. A calculation was made where $\log \beta_5$ and $\log \beta_6$ were kept constant in the two media, and had values determined in the range $Z_n \leq 5$. Assuming the deviations from the model $\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_n^{2+}$, ($n = 1 \dots 6$) to be due to an error in C , a good fit is obtained with corrections in C (usually < 0.5 %, cf. Table 2), which would seem to be reasonable, considering the experimental conditions. It is worth noticing that variations in K_a give K_a -values in very good agreement with those separately determined.

Calculations assuming mixed or polynuclear complexes were also carried out, but these calculations gave no further improvements.

Obviously the present complementary measurements and analysis at $Z_n > 4$ strongly confirmed the results earlier published. It has been clearly established that the effects at high Z_n -values cannot be explained solely by analytical or experimental errors. Additional complex formation must be taken into account. There is evidence for the formation of both the complexes $\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_5^{2+}$ and $\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_6^{2+}$.

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Fatty Acid Composition of the Seed Fats of a Few Vacciniaceae and Empetraceae

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No previous studies of fatty acids from seeds of plants belonging to the families Vacciniaceae and Empetraceae have been recorded.¹ As to the related family Ericaceae, (occasionally considered as including Vacciniaceae), a single analysis on *Arctostaphylos glauca* has been published,² cf. Table 1.

Table 1. Fatty acid composition of the seed oils (weight %).

Acid	<i>Vaccinium uliginosum</i>	<i>Oxycoccus quadripetalus</i>	<i>Empetrum nigrum</i>	<i>Arctostaphylos glauca</i> ^a
Palmitic	1.1	5	3	} 6
Stearic	0.2	1.5	0.5	
Oleic	23	21	14	32
Linoleic	46	36	42	33
Linolenic	29	36	40	25
Oil content	30 %	20 %	8 %	56 %

^a Literature values (Ref. 2).

The present study was performed on berries of *Vaccinium uliginosum*, *Oxycoccus quadripetalus* and *Empetrum nigrum*, collected near Lodbjerg light-house, Denmark, in August 1966. The kernels were isolated and after crushing extracted with light petroleum (b.p. 40–60°) in a Soxhlet apparatus as described;³ the oil contents of the seeds appear from Table 1. After saponification of the glycerides with ethanolic KOH, and acidification with H₂SO₄, the fatty acids were isolated by extraction with Et₂O and converted into methyl esters by reaction with CH₂N₂. The esters were chromatographed on an Aero-graph instrument, model 1520, equipped with a heat conductivity detector, using a polar stationary phase (DEGS) as well as a nonpolar phase (E 301). Assuming the areas under the recorded curves to be proportional to the molar percentages of the individual components, the compositions listed in Table 1 were determined (as weight per cent of the fatty acid mixture).

The identity of the individual fatty acids has been further verified by mass spectrom-

etry. The methyl ester mixtures were investigated on a GLC/MS-instrument (Perkin-Elmer model 270) at 70 eV and an ion source pressure of 3×10^{-6} torr. The spectra obtained were in accordance with those reported⁴ as well as with spectra of authentic specimens. Obviously, the three oils investigated all belong to the group of fats classified by Hilditch⁵ as rich in linolenic and linoleic acid.

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