Komaroffia Oils – An Excellent New Source of Δ5-Unsaturated Fatty Acids

Sir:

In continuation of our earlier work on *Nigella* (1) and our search for new sources of γ-linolenic acid (2–4), additional species of genus *Nigella* were also investigated. Surprisingly, two of the *Nigella* species deviated strongly from the fatty acid pattern found in all the other *Nigella* species. The deviating ones were those which were formerly considered to be a separate genus *Komaroffia* (5), but were now combined with *Nigella* in other botanical monographs (6). The seed oils of these two species showed a totally different fatty acid composition. The major fatty acids were Δ5-fatty acids at a combined level of more than 60% of total fatty acids and including the highest ever reported level of 20:3Δ5*cis*,11*cis*,14*cis*.

Δ5-Fatty acids are known to be phylogenetically very old, and they are found in many early forms of life, including lower marine organisms (7). They are also present in very old plants such as *Equisetum* and *Ginkgo* (7,8), in nearly all gymnosperms, and in a handful of angiosperm plant families. In particular, the Δ5*cis*-non-methylene-interrupted polyenoic (NMIP-) fatty acid 20:3Δ5*cis*,11*cis*,14*cis,* an arachidonic acid analog with the Δ8 double bond missing, has been postulated to be a very archaic fatty acid (7). This acid, however, appears to have been gradually eliminated during the later evolutionary processes leading from one branch of the Gymnospermae to the higher Angiospermae, where this Δ5-NMIP acid has been found so far only in the rather archaic plant family Ranunculaceae (7,9,10).

Seed samples of *Nigella bucharica* and *N. integrifolia* (synonym: *Komaroffia diversifolia*) were obtained through the courtesy of Prof. U. Jensen, Department of Botany, University of Bayreuth, Germany. Standardized fatty acid "fingerprints" were obtained as described (11), using gas–liquid chromatography (GLC) of the fatty acid methyl esters on capillary columns of Silar 5CP. Fatty acid methyl ester peaks were identified by comparison and co-chromatography with standards and with oils of known composition (containing a variety of Δ5-fatty acids) that had been encountered in earlier phases of the present study (4,10,12).

Figure 1 shows standardized capillary GLC seed oil "fatty acid fingerprints" (11) as they are regularly obtained during the course of our screening work for α-linolenic acid, and which can often be used as a chemotaxonomic criterion. Shown in Figure 1 are the fingerprints of *N. bucharica*, *N. integrifolia*, *N. hispanica,* and *Caltha palustris*. As usual in our fingerprints, regular fatty acids (those occurring in most edible oils) are not labeled but unusual peaks are labeled as in References 10 and 11 (see figure caption for numbers). The postulated relation typical for all *Nigella* species (1), a peak size ratio of 12 >> 10, can be seen in all the *Nigella* and *Komaroffia* species. In *Komaroffia*, however, there is an additional, much larger peak 13 which elutes after peak 12. This is the major Δ5-NMIP fatty acid, 20:3Δ5*cis*,11*cis*,14*cis,* which is identical to one of the major fatty acids found in *Caltha*, in many Gymnospermae, and in some other genera of the Ranunculaceae (7,9,10,12). The gas chromatographic behavior of this acid and of 18:1Δ5*cis* (peak 5 in Fig. 1) is well known from previous investigations (4,10).

Nigella (Komaroffia) integrifolia contained the following Δ5*cis* fatty acids: 16:1Δ5*cis*, 2.2% of total fatty acids; 18:1Δ5*cis*, 34.6%; 20:1Δ5*cis*, 0.5%; 20:2Δ5*cis*, 0.2%; and 20:3Δ5*cis*, 28.8%. *Nigella (Komaroffia) bucharica* contained 16:1Δ5*cis,* 2.8%; 18:1Δ5*cis,* 33.0%; 20:1Δ5*cis,* 0.6%; 20:2Δ5*cis,* 0.2%; and 20:3Δ5*cis,* 29.9%. This means that the two *Nigella (Komaroffia)* species are now the source of the highest known amounts of 20:3Δ5*cis*,11*cis*,14*cis* in nature, and the source of the second-highest known amounts of 18:1Δ5*cis.* As Figure 1 and our earlier work (1) show, all the *Nigella* s.str. species investigated so far do not contain Δ5*cis* fatty acids. For other quantitative data, and for the fatty acid contents of *Caltha,* which is also shown in the "fingerprints" of Figure 1, the reader is referred to the literature (1,9).

Our earlier investigations in the plant family Ranunculaceae (1,3,10,12) showed that the seed oil fatty acid patterns, or "fingerprints", are highly genus-specific, i.e., they are very characteristic for a given plant genus (actually, so much so that "fingerprints" like those in Fig. 1 could be used in a way similar to "leaf shape" in botanical taxonomy). This means that plant species belonging to one and the same genus usually show the same fatty acid pattern or "fingerprint". On the other hand, the genus-to-genus differences in fatty acid patterns are often very large. In our earlier investigations of *Nigella,* the results also followed the same rule. It was therefore very surprising that the two *Nigella* spp. seed oils analyzed here should deviate so strongly from those of all the other species of genus *Nigella* investigated so far. However, older authors had claimed that the two species in question here (*N. integrifolia* and *N. bucharica*) were members of a different and separate genus *Komaroffia* (5). Our old observation that, as a rule in the Ranunculaceae, genus-to-genus differences were large whereas species-to-species differences were insignificant (10) would still hold if the two species in

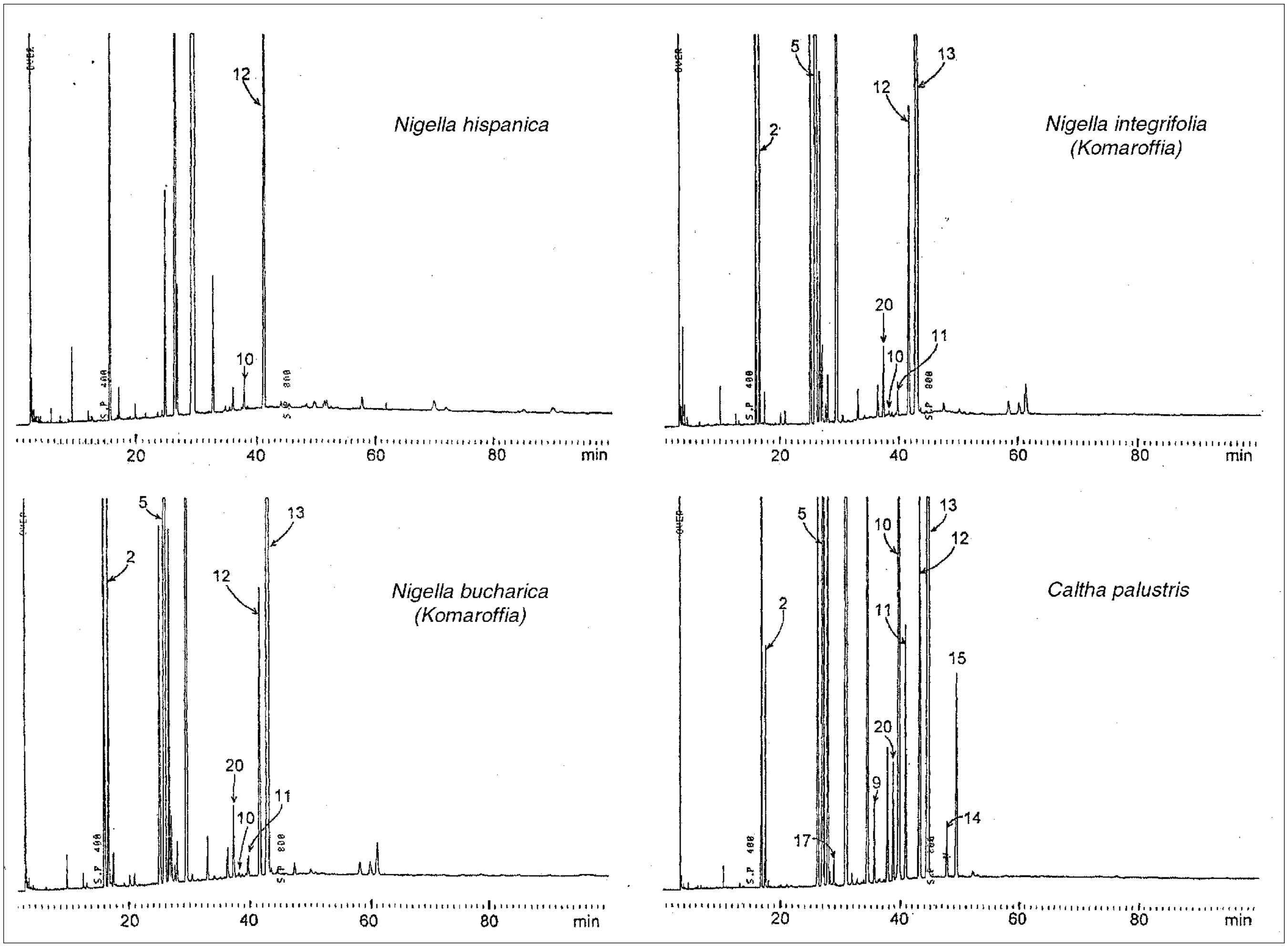

FIG. 1. Standardized capillary gas–liquid chromatographic "seed oil fatty acid fingerprints" (11) (as used in plant chemotaxonomy) of *Nigella hispanica, N. integrifolia, Caltha palustris,* and *N. bucharica* (clockwise). Peak numbers assigned as in references 10, 11. As usual for these fingerprints, only the chemotaxonomically (or phylogenetically) relevant fatty acids have been labeled. The labeled peaks are: 2 = 16:1Δ5*cis*; 5 = 18:1Δ5*cis*; 9 = 18:4Δ5*cis*,9*cis*,12*cis*,15*cis*; 10 = 20:1n-9 (equal to 20:1Δ11*cis*); 11 = 20:2Δ5*cis*,11*cis*; 12 = 20:2n-6 (equal to 20:2Δ11*cis*,14*cis*); 13 = 20:3Δ5-*cis*,11*cis*,14*cis*; 14 = 20:3Δ11*cis*,14*cis*,17*cis*; 15 = 20:4Δ5*cis*,11*cis*,14*cis*,17*cis*; 17 = 18:2Δ5*cis*,9*cis*; and 20 = 20:1Δ5*cis*.

question here would continue to be regarded as a separate genus *Komaroffia*, i.e., different from *Nigella*.

Our findings regarding *Komaroffia* oil, combined with the fact that these annual plants could easily be grown in temperate climates such as Central and Eastern Europe or the United States, make these an interesting potential source for Δ5-fatty acids. The two *Nigella* subgenus *Komaroffia* species grow in the more arid regions of Central Asia. If an industrial or pharmaceutical interest in Δ5-fatty acids should develop, be it as a raw material or as a chemical intermediate, they could probably be developed as a new annual crop for the more arid parts of Europe and North America, or they could serve as sources for genes or information in gene transfer and enzyme design. Other major sources (>50%) of Δ5 fatty acids have been described in angiosperm seed oils. With the exception of *Limnanthes*, however, these would be more difficult crops in northern climates, because they are either perennial plants or tropical lianas. They all, however, could possibly serve as sources of genes which code for enzymes that participate in the biosynthesis of Δ5-fatty acids.

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Kurt Aitzetmüller,
Institute for Chemistry and Physics of Lipids,
BAGKF, Piusallee 76, D-48147 Münster, Germany.
E-mail: aitzetm@uni-muenster.de