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# STEAM VOLATILE CONSTITUENTS FROM LEAVES OF *RHUS TYPHINA**

HANS-JÜRGEN BESTMANN, BEATE CLASSEN, UWE KOBOLD, OTTO VOSTROWSKY, FRED KLINGAUF† and URSULA STEIN†

Department of Organic Chemistry, University Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen F.R.G.; †Federal Biological Research Centre, Institute for Biological Pest Control, Heinrichstrasse 243, D-6100 Darmstadt, F.R.G.

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**Key Word Index**—*Rhus typhina*; Anacardiaceae; volatile constituents; GC/MS analysis; insecticidal properties.

**Abstract**—The steam distillate from leaves of the Buck's horn, *Rhus typhina*, displayed insecticidal properties against aphids. GC and GC/MS analysis of the distillate resulted in the identification of more than 70 constituents, comprising among others terpenoids, hydrocarbons, aldehydes, fatty acids and *m*-substituted long chain alkylphenols.

## INTRODUCTION

As a part of our systematic studies on the insecticidal activities of the essential oils and ethanolic extracts from more than 200 plants from various families [2, 3], we now report on the composition and insecticidal properties of the steam-volatile constituents from the leaves of the Buck's horn, *Rhus typhina* L. (Anacardiaceae; German: Essigbaum, Hirschkolbensumach; French: Vinsigrier).

*Rhus typhina* is a 3–6 m high shrub; its leaves, 20–30 cm long, consist of unpaired serrated or lacerated leaflets, which turn bright red in autumn. The Buck's horn originates from the eastern part of Northern America and is found as an ornamental shrub in parks and gardens in Europe [4]. The plant is reported to be non-toxic to humans [5] or only weakly toxic when eaten, resulting in stomach and digestive complaints [4]. Unlike Poison oak, *R. toxicodendron* L., which produces acute dermatitis upon the slightest contact of exposed skin with the leaves or other parts of the plant [5], *R. typhina* produces no skin irritant. Because of this, it is also called 'non poisonous sumach'. The fruits are even used for lemonade production [5].

The steam distillate, ethanol extracts and other extracts from leaves of *R. typhina* display insecticidal properties towards aphids. Since there are no reports in the literature about the volatile constituents of *R. typhina*, a GC and GC/MS analysis of a steam distillate from the leaves was carried out, in an effort to identify the insecticidal components.

## RESULTS AND DISCUSSION

From 500 g of freshly harvested leaves (including the petioles), 27 mg (0.005%) of a malodourous solid was obtained by steam distillation.

### *Analysis of the essential oil*

A pentane solution of the *R. typhina* oil was analysed by GC and GC/MS. More than 70 components were identified by their mass spectra as well as by their Kováts' retention indices (Table 1).

Of the monoterpenes, only a small number of alcohols in low concentration were found: *p*-menthadien-7-ol (**9**), linalool (**10**), terpineol (**13**) and geraniol (**15**). The main sesquiterpene hydrocarbon characterized was caryophyllene (**23**), followed by δ-cadinene (**29**), γ-cadinene (**28**), α-muurolene (**27**), humulene (**24**), α-copaene (**19**), and α-*trans*-β-bergamotene (**25**) in order of decreasing concentration, respectively. Five other sesquiterpene hydrocarbons ($C_{15}H_{24}$) were found, the structures of which could not be identified. Furthermore, three sesquiterpenoid oxygen compounds ($C_{15}H_{26}O$) were found, **32** being identified as torreyol from its very characteristic mass spectrum [6].

One of the most abundant components was the diterpene alcohol, phytol (**48**), which was accompanied by its oxidation product, hexahydrofarnesyl acetone (**39**) (Table 1).

The signals of compound **52**, **53** and **59** were assigned with *m*-tridecenylphenol (**52**), *m*-tridecylphenol (**53**) and *m*-pentadecenylphenol (**59**), respectively. The *meta*-substitution pattern was established unequivocally by mass spectrometry [7].

Long chain, alkyl-substituted phenols are characteristic constituents of Anacardiaceae [8]. For example, Cardanol (= Anacardol), a mixture of 3-pentadecylphenol, 3-(8-pentadecenyl)phenol, 3-(8,11-pentadecadienyl)phenol and 3-(8,11,14-pentadecatrienyl)-phenol [9], was isolated from the pericarp of the fruits of the Kidney bean of Malacca, *Semecarpus anacardium* L. [10], and the peel of Cashew nuts, *Anacardium occidentale* L. [11]; Urushiol (= Toxicodendrine, 'Rhus poison') and Cardol are found in *R. toxicodendron* [12] as well as in *A. occidentale* [13]. These constituents, being mixtures of substituted phenols, brenzcatechols and resorcinols, represent the toxic principals of these plants, the latter two being potent skin irritants.

While *m*-alkylphenols with a $C_{15}$-side chain are frequently found in Anacardiaceae, *m*-alkylphenols with a tridecyl side chain have been found only in *Ginkgo biloba* L. [14] and the brown alga *Caulocystis cephalornithos* Knetz [15]. The unsaturated *m*-tridecenylphenol **52**

* Part V in the series 'Herbal Insecticides' [1].

Table 1. Constituents of the essential oil from leaves of *R. typhina*

| Nos | Compound | % total (FID) | Ret. index (SE 54) | Method of identification* |
|---|---|---|---|---|
| 1 | Heptane | 0.002 | 700 | m, i |
| 2 | Octane | 0.04 | 800 | m, i |
| 3 | Furfural | 0.03 | 828 | m |
| 4 | 3-Hexen-1-ol | 0.72 | 851 | m |
| 5 | Nonane | 0.03 | 900 | m, i |
| 6 | Decane | 0.21 | 1000 | m, i |
| 7 | 2-Octenal | 0.04 | 1048 | m, i, h |
| 8 | Octan-1-ol | 0.07 | 1069 | m |
| 9 | *p*-Menthadien-7-ol | 0.25 | 1075 | m |
| 10 | Linalool | 0.85 | 1100 | m, i |
| 11 | Nonanal | 1.31 | 1104 | m, i, h |
| 12 | 2-Nonenal | 0.04 | 1154 | m, i, h |
| 13 | Terpineol | 0.25 | 1190 | m, i |
| 14 | Decanal | 0.11 | 1206 | m, i, h |
| 15 | Geraniol | 0.19 | 1255 | m, i |
| 16 | 2-Decenal | 0.17 | 1260 | m, i, h |
| 17 | tridecane | 0.03 | 1300 | m, i |
| 18 | Undecanal | 0.34 | 1308 | m, i, h |
| 19 | α-Copaene | 0.66 | 1379 | m, i |
| 20 | 2-Undecenal | 0.01 | 1386 | m, i, h |
| 21 | Tetradecane | 0.14 | 1400 | m, i |
| 22 | Dodecanal | 0.27 | 1413 | m, i, h |
| 23 | Caryophyllene | 6.30 | 1422 | m, i |
| 24 | Humulene | 0.10 | 1461 | m, i |
| 25 | α-*trans*-β-Bergamotene | 0.22 | 1496 | m |
| 26 | Pentadecane | 0.13 | 1500 | m, i |
| 27 | α-Muurolene | 0.50 | 1509 | m, i |
| 28 | γ-Cadinene | 0.63 | 1525 | m, i |
| 29 | δ-Cadinene | 2.14 | 1533 | m |
| 30 | Dodecanoic acid | 0.10 | 1562 | m, i |
| 31 | Hexadecane | 0.10 | 1600 | m, i |
| 32 | Torreyol | 0.41 | 1656 | m |
| 33 | Tetradecan-1-ol | 0.35 | 1678 | m, i |
| 34 | Heptadecane | 0.01 | 1700 | m, i |
| 35 | Pentadecanal | 0.26 | 1720 | m, i, h |
| 36 | Tetradecanoic acid | 3.22 | 1773 | m, i |
| 37 | Octadecane | 0.21 | 1800 | m, i |
| 38 | Hexadecanal | 0.02 | 1819 | m, i, h |
| 39 | Hexahydrofarnesyl acetone | 0.38 | 1846 | m |
| 40 | Pentadecanoic acid | 0.08 | 1862 | m |
| 41 | Benzyl salicylate | 0.19 | 1881 | m |
| 42 | Hexadecan-1-ol | 0.05 | 1890 | m |
| 43 | Heptadecanal | 0.20 | 1913 | m, i, h |
| 44 | Phytol isomer | 3.55 | 1944 | m |
| 45 | Hexadecanoic acid | 11.06 | 1973 | m |
| 46 | Octadecanal | 0.11 | 2012 | m, i, h |
| 47 | Octadecan-1-ol | 0.16 | 2090 | m |
| 48 | Phytol | 31.85 | 2110 | m |
| 49 | Octadecanoic acid | 0.26 | 2178 | m |
| 50 | Docosane | 0.14 | 2200 | m, i |
| 51 | Eicosanal | 0.05 | 2229 | m, i, h |
| 52 | *m*-Tridecenylphenol | 0.02 | 2283 | m |
| 53 | *m*-Tridecylphenol | 0.05 | 2294 | m |
| 54 | Eicosan-1-ol | 3.60 | 2296 | m |
| 55 | Tricosane | 0.48 | 2300 | m, i |
| 56 | Henelcosanal | 0.02 | 2333 | m, i, h |
| 57 | Tetracosane | 0.26 | 2400 | m, i |
| 58 | Docosanal | 0.10 | 2430 | m, i, h |
| 59 | *m*-Pentadecenylphenol | 0.02 | 2495 | m |
| 60 | Docosan-1-ol | 0.70 | 2497 | m |
| 61 | Pentacosane | 2.04 | 2500 | m, i |

Table 1. *Continued*

| Nos | Compound | % total (FID) | Ret. index (SE 54) | Method of identification* |
|---|---|---|---|---|
| **62** | Tricosanal | 0.11 | 2530 | m, i, h |
| **63** | Hexacosane | 0.15 | 2600 | m, i |
| **64** | Tetracosanal | 0.47 | 2632 | m, i, h |
| **65** | Heptacosane | 1.11 | 2700 | m, i |
| **66** | Pentacosanal | 0.17 | 2733 | m, i, h |
| **67** | Octacosane | 0.06 | 2800 | m, i |
| **68** | Hexacosanal | 0.71 | 2830 | m, i, h |
| **69** | Nonacosane | 0.20 | 2900 | m, i |
| **70** | Heptacosanal | 0.15 | 2930 | m, i, h |
| **71** | Triacontane | 0.05 | 3000 | m, i |
| **72** | Octacosanal | 0.30 | 3032 | m, i, h |

*m, mass spectrum; i, retention index or co-chromatography; h, dimethyl hydrazone mass chromatography.

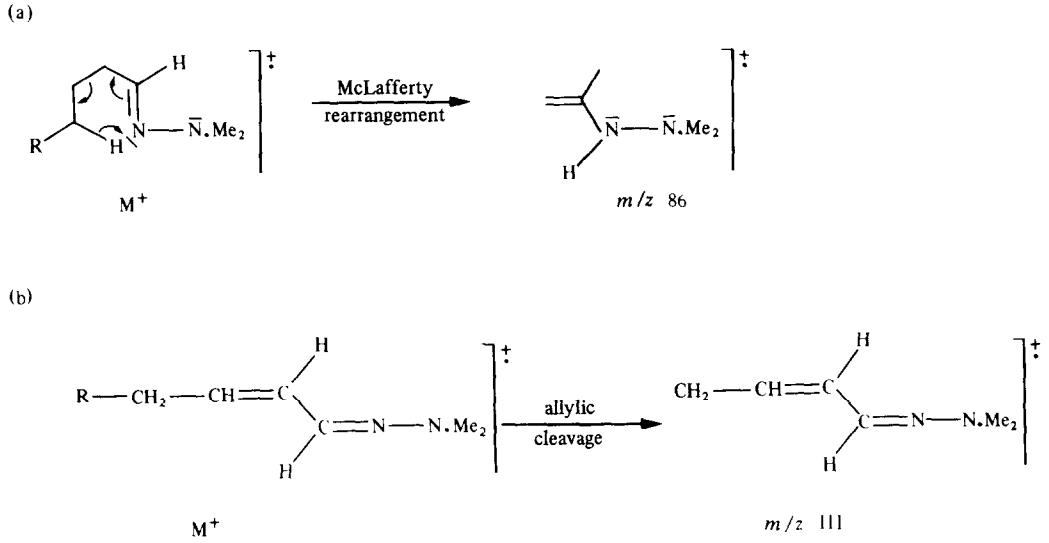
found in this analysis has not been previously reported as a plant constituent.

Most of the constituents of *R. typhina* seem to originate from fat metabolism. Among them, the fatty acids dodecanoic (**30**), tetradecanoic (**36**), pentadecanoic (**40**), hexadecanoic (**45**) and octadecanoic acid (**49**) were identified. Almost the complete series of *n*-hydrocarbons from heptane (**1**) to triacontane (**71**) was found.

In addition, long chain aldehydes were identified in the essential oil. Since the structure elucidation of aldehydes by mass spectroscopy is not easy (because of uncharacteristic spectra), a TLC fraction ($d_3$, see next section) containing aldehydes only, was taken for analysis. A small sample of the oil was reacted with *N,N*-dimethylhydrazine (DMH) to convert the aldehydes into the corresponding hydrazones. These *N,N*-dimethylhydrazones are volatile enough for GC/MS analysis and can be detected very easily by mass spectroscopy [16]. The hydrazones of saturated aldehydes give rise to a very significant fragmentation ion (*m/z* 86) though McLafferty rearrangement (Scheme 1, part a)). This together with an intense molecular ion make the hydrazones especially suitable for GC-MS analysis.

Figure 1 shows the mass chromatograms used for the identification of hydrazones obtained from TLC fraction $d_3$. The upper most recorder trace is the reconstructed gas chromatogram (RGC) of the fraction, the second trace the mass chromatogram for the ion *m/z* 86, representing the characteristic fragment for the derivatives of saturated aldehydes. The traces below are the mass chromatograms of the molecular ions of the *N,N*-dimethyl alkylhydrazones (e.g. *m/z* 184 for nonyl, *m/z* 198 for decyl, *m/z* 212 for undecyl, etc.) By superimposing the ion signals for *m/z* 86 with these molecular ion chromatograms, it was possible to show the presence of n-nonanal (**11**) to octacosanal (**72**) in TLC fraction $d_3$ of the essential oil of *R. typhina*.

α,β-Unsaturated aldehydes react with DMH to form the corresponding α,β-unsaturated hydrazones. These hydrazones cannot undergo McLafferty rearrangement to




Scheme 1. Fragmentation ions of hydrazones of saturated aldehydes (a) and α,β-unsaturated aldehydes (b).

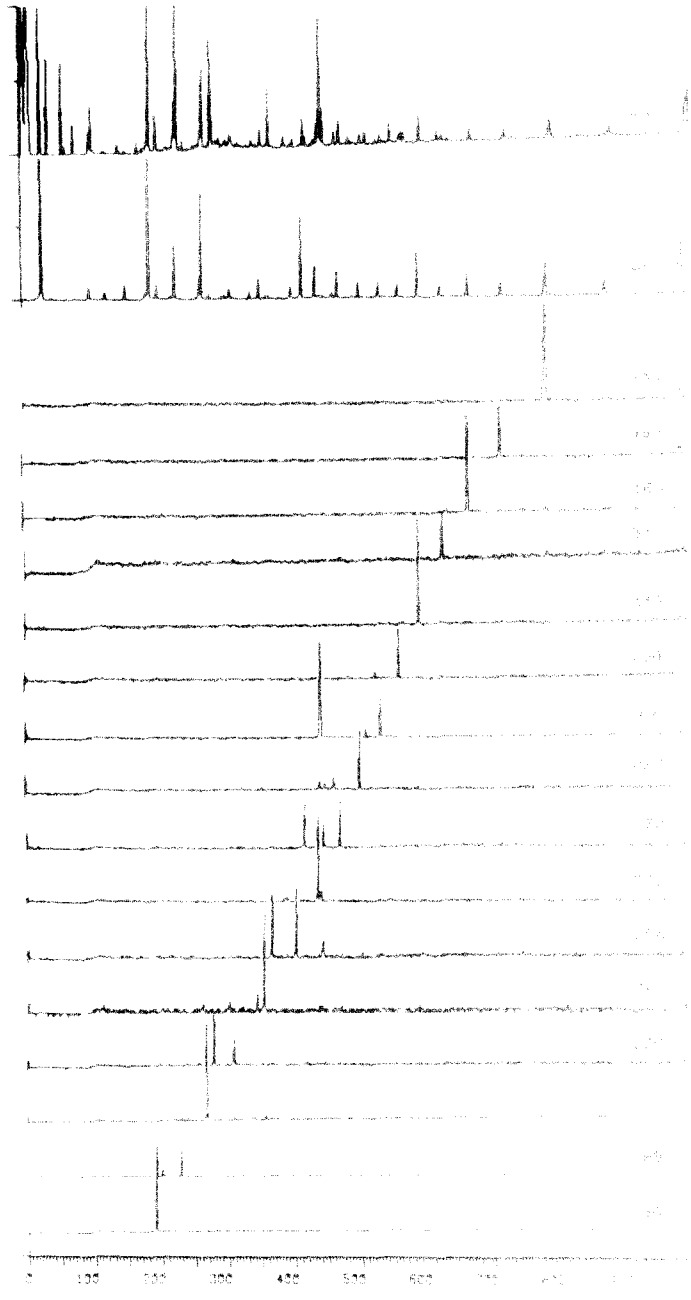


Fig. 1. Mass chromatographic identification of the *N,N*-dimethyl alkylhydrazones of the saturated aldehydes obtained from TLC fraction $d_1$ (RGC = reconstructed gas chromatogram, mass chromatograms at $m/z$ 58 ($CH_2$=$NH$-$N(Me)_2$) and M$^+$ for aldehydes $C_{\quad}$–$C_{\quad}$).

the fragment $m/z$ 86 anymore. Instead the ionized molecules simply undergo allylic cleavage leading to fragment $m/z$ 111 (Scheme 1, part b)). The presence of this fragment ion in combination with the corresponding molecular ions led to the identification of 2-octenal (**7**), 2-nonenal (**12**), 2-decenal (**16**) and 2-undecenal (**20**) in *R. cyphina* (Table 1).

Finally, furfural (**3**), 3-hexen-1-ol (**4**), octan-1-ol (**8**), tetradecan-1-ol (**33**), hexadecan-1-ol (**42**), octadecan-1-ol (**47**), eicosan-1-ol (**54**), docosan-1-ol (**60**), and benzyl salicylate (**41**) were identified. These compounds are common plant constituents, frequently found in essential oils and plant extracts (Table 1).

None of the compounds mentioned above has been previously characterized as a constituent of *R. cyphina* and many of them were shown to be components of Anacardiaceae species.

*Insecticidal properties of R. cyphina oil*

Buck's horn is naturally free of any plant diseases and

Table 2. Insecticidal effect of an ethanolic extract of *R. typhina* on three economically important aphid species

| Year | Mean mortality rates [%]* recorded 24 hr after treatment | | |
|---|---|---|---|
| | *M. persicae* | *M. dirhodum* | *A. fabae* |
| 1986† | 74.1 | 70.9 | 64.7 |
| 1985‡ | 96.3 | 90.9 | 48.3 |

*Corrected values after Sun and Shepard [20].

†Numerical counts based on 150–350 aphids/species/pot with 10 replicates each.

‡Mortality rates for 1985 based on estimation with 2–3 replicates each.

Table 3. Constituents of TLC fraction $d_5$, displaying 72% mortality for *M. dirhodum*

| Terpenoid compounds (%) | Aliphatic alcohols (%) | Fatty acids (%) |
|---|---|---|
| 25.2 Phytol | 15.0 1-Docosanol | 12.4 Hexadecanoic acid |
| 13.1 Linalool | 4.6 1-Tetradecanol | 7.1 Tetradecanoic acid |
| 1.6 Myrcenol* | 2.1 1-Eicosanol | 1.8 Dodecanoic acid |
| 1.3 Geraniol | 1.2 1-Octadecanol | 0.5 Octadecanoic acid |
| 0.3 Phytol isomer | 1.2 1-Octanol | 0.1 Nonanoic acid* |
| | 0.3 1-Hexadecanol | 0.1 Decanoic acid* |

*Only found after TLC enrichment.

pests. Ethanolic Soxhlet extracts of *R. typhina* (20 g fresh leaves extracted with 150 ml 96% ethanol) showed remarkable aphicidal properties when applied to potted wheat plants infested by the rose grain aphid, *Metopolophium dirhodum* (Walk.), to Brussels sprouts infected with the green peach aphid, *Myzus persicae* (Sulz.), and to broad bean infected with black bean aphid *Aphis fabae* Scop. The mortality of aphids 24 hr after treatment showed values between 65 and 74%. The highest mortality rate was recorded in *M. persicae*, whereas *A. fabae* proved to be the least susceptible (Table 2). Similar results have been obtained with corresponding extracts of leaves from the mango tree (*Mangifera indica* L.), another member of the Anacardiaceae family.

The promising results with the ethanolic extract of *R. typhina* led to further research on the constituents of the Buck's horn.

Pentane solutions of 2, 1, 0.5 and 0.25%, 1 ml each, from the steam distillate were sprayed onto wheat plants infested with the rose grain aphid, *M. dirhodum*. After 48 hr the remaining infestation of the plant by aphids was checked and a mortality rate of 98, 96, 84 and 62% determined for the respective solutions.

To assign the insecticidal activity from the essential oil of *R. typhina* to one single compound or at least one class of compounds, the oil was fractionated by TLC, and each fraction tested for its insecticidal properties (see Experimental). After four different TLC separations, each using a different solvent, two insecticidal fractions were isolated ($d_3$, $R_f$ 0.58–0.72 and $d_5$, $R_f$ 0.22–0.38), showing a mortality rate of 70 and 72%, respectively, for *M. dirhodum*. All the other fractions had activities ranging from 12 to 55%, only. Fraction $d_3$ (see Experimental) consisted almost only of saturated and $\alpha,\beta$-unsaturated aldehydes and hexahydrofarnesyl acetone (**39**) (see Fig. 1). Fraction $d_5$, which was a little more effective, contained alcohols and carboxylic acids only (Table 3).

Furthermore, in fraction $d_5$ only a trace of *m*-pentadecenylphenol (**59**) was found, whereas the bulk of the three *m*-substituted alkylphenols **52**, **53** and **59** was found in the low activity fraction $d_4$ (mortality rate 53%). Thus, these typical *Rhus* components, which are responsible for the toxic and skin irritant effects, could be ruled out as the insecticidal principle of the plant oil. The six main constituents, namely phytol (**48**), linalool (**10**), tetradecanol (**33**), docosanol (**60**), tetradecanoic acid (**36**) and hexadecanoic acid (**45**), were tested individually, in the same concentrations as those found in TLC fraction $d_5$ for insecticidal activity; none of the components exhibited the same activity as that of the whole fraction. However, a synthetic mixture of the six components, in the proportions found in fraction $d_5$, gave the same mortality rate as that of the TLC-fraction. This may be a synergistic or additive effect and will be investigated in future studies.

## EXPERIMENTAL

*Steam distillation.* 500 g of freshly harvested leaves of *R. typhina* in 1 l $H_2O$ were subject to continuous steam distillation in an apparatus similar to Sprecher [17] for 16 hr. The steam volatile substances were extracted with 1 ml pentane.

*GC.* Capillary GC was performed on a Hewlett-Packard 5890A gas chromatograph equipped with a Shimadzu Chromatopac C-R3A data system. Injector 240°, FID 260°, split injection. FSCC SE54 (25 m × 0.25 mm), temp. 2 min at 60°, 60–260° at 6°/min. Carrier gas $N_2$, 22 cm/sec linear gas velocity.

*GC/MS.* A Finnigan 9502 gas chromatograph linked to a Finnigan 3200E quadrupole mass spectrometer with a Data System 6000 was used. Column and temp. progr. as above, carrier gas He, 70 eV EI spectra, 2 sec/scan.

Mass spectra were compared with those from authentic samples and from the literature [6, 18, 19]. The retention indices were determined by ref. compounds and compared with those from previous publications.

*TLC fractionation of the oil.* The essential oil was fractionated by using four consecutive separation steps (i–iv), in which only those fractions showing insecticidal activity were rechromatographed (Silica gel 60, 0.2 mm, for separations i–iii, and 1 mm for iv). Separation (i) *n*-pentane (× 5 developments), (ii) *n*-pentane (× 3), followed with pentane–$Et_2O$ (19:1) (× 2); (iii) pentane and then pentane–$Et_2O$ (19:1) followed by pentane–$Et_2O$ (9:1), and pentane–$Et_2O$ (4:1); (iv) as step (i). This procedure gave two insecticidal fractions, $d_3$, $R_f$ 0.58–0.72, and $d_5$, $R_f$ 0.22–0.38.

*Insecticidal test.* (a) *Soxhlet extract*: one day prior to the test five to six young potted wheat plants (8–10 cm high) per pot were infested with 150–200 individuals of the rose grain aphid, *Metopolophium dirhodum* (Walk.). In the case of the green peach aphid, *Myzus persicae* (Sulz.), and the black bean aphid, *Aphis fabae* Scop., singly potted hostplants were infested 4–5 and 3–4 days prior to the test, respectively, yielding 250–350 aphids on Brussels sprouts (15 cm high) and 300–400 individuals on broad bean (30 cm high) per plant.

The exact number of aphids per pot was recorded 1 hr before the plants were used in the test. By using a perfume spray-diffuser the EtOH extract of *R. typhina* or EtOH (96%) only (control) were sprayed onto the plants until runoff; 1.5–2.0 ml of the test solns/pot were used on the wheat plants and 3.0–3.5 ml/pot on Brussels sprouts and broad bean. 24 hr later the number of live aphids was counted and thus the mortality rate determined. (b) *Steam distillate fractions*. two–four young wheat plants (12–15 cm high) infested with the rose grain aphid *Metopolophium dirhodum* (Walk.) (*ca* 100 insects/test), were cut off and stuck into a small vial filled with water. The number of aphids per plant was recorded. Then 1 ml of each of the test solns was sprayed on to the plants using a perfume spray-diffuser. After 16 hr the number of live aphids was counted and thus the mortality rate determined.

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