

Research Paper

Esters of calendula oil and tung oil as reactive diluents for alkyd resins

Ursula Biermann¹, Werner Butte¹, Ralf Holtgreffe², Willi Feder² and Jürgen O. Metzger^{1,3}¹ University of Oldenburg, Department of Pure and Applied Chemistry, Oldenburg, Germany² biopin, Jever, Germany³ abiosus e.V., Oldenburg, Germany

A simple protocol for the transesterification of highly unsaturated vegetable oils such as calendula oil and tung oil, catalyzed by sodium methoxide, is described. Calendula oil contained about 59–65% of calendic acid (8,10-*trans*,12-*cis*-octadecatrienoic acid) (**1a**), and tung oil about 84% of α -eleostearic acid (9-*cis*,11,13-*trans*-octadecatrienoic acid) (**2a**). Transesterifications of calendula oil with alcohols such as methanol, ethanol, and isopropanol give the respective calendula oil esters, which were tested as reactive diluents for alkyd resins in coating formulations. Especially ethyl and isopropyl calendula oil esters showed good properties, including low viscosity and good drying performance. Furthermore, a shortening of the drying time of about 35–40% compared to conventionally prepared formulations was achieved. Analogously, the respective esters of tung oil were synthesized and used as reactive diluent.

Keywords: α -Eleostearic acid esters / Calendic acid esters / Calendula oil / Reactive diluent / Renewable raw material / Tung oil

Received: June 25, 2009; accepted: October 5, 2009

DOI 10.1002/ejlt.200900142

1 Introduction

Due to the serious problem of emissions of volatile organic chemicals (VOC) into the atmosphere, the development of products of the chemical industry that can be processed with reduced amounts of organic solvents, or even without solvents, is a great challenge [1]. At present, it is estimated that the use of organic solvents mainly in the processing industry makes up more than half of the total emissions in Germany. Germany has to reduce the VOC emissions by about 350,000 t/a. The main emissions are caused in coating, printing inks, and adhesive processing [2].

Alkyd resins are basic materials in the coating processing and used as binders to form a tough, continuous film [3]. The global production amounts to about 1 Mio t/a. Alkyd resins are polyesters produced by condensation polymerization of three types of monomers: polyols, polybasic acids and fatty acids or triacylglycerols. The triacylglycerols used are mostly drying plant oils, *e.g.* linseed oil [4]. The choice and amount of

the oil in the alkyd resin determines the drying rate and the solubility of the polymer in organic solvents. Alkyd resins are viscous, tacky materials that are difficult to handle. Most often, these handling problems are overcome by dissolving the resins in organic solvents, which evaporate into the atmosphere as VOC, giving rise to regulations. This is a most important problem with alkyd resins as binders. In Germany, the coating processing is the most important VOC emitter.

The development of products in the coating processing that can be processed without the use and emission of VOC would be an important contribution to sustainable development. This contribution would be increased if these products could be produced from renewable raw materials [5, 6]. There are already some examples for VOC-reduced coatings, such as high-solid coatings, water-diluted coatings [3], powder coatings, and radiation-hardening coating systems [7].

A patent by DSM describes a resin composition containing an alkyd resin and a reactive diluent. The reactive diluent is an alkyl ester – preferentially a methyl ester derived from the acid of an unsaturated vegetable oil such as tung oil or calendula oil serving as a solvent – and is incorporated into the film while curing [8].

Already in 1987, calendula was proposed as new oil crop for the chemical industry [9]. In the EU project entitled

Correspondence: Ursula Biermann, University of Oldenburg, Department of Pure and Applied Chemistry, 26111 Oldenburg, Germany.

E-mail: ursula.biermann@uni-oldenburg.de**Fax:** +49 798 193718

“Calendula as Agronomic Raw Material for Industrial Applications” (CARMINA), the cultivation and usage was developed. It was reported that “alkyd paints with less volatile organic compounds (VOC) and non-fogging polyurethane foams (PUF) can be produced with calendula oil as raw material and their use would reduce VOC-emissions” [10]. Calendula oil is becoming commercially available [11]. Tung oil is imported from China and Brazil. However, the tung oil market is not stable and the price of tung oil is subject to seasonal fluctuations. A sustainable supply would be desirable. Calendula oil could stabilize the market.

Calendic acid (8,10-*trans*,12-*cis*-octadecatrienoic acid) (**1a**) is the main fatty acid, with a content of up to 65% in the seed oil of *Calendula officinalis* L. (Compositae) (Fig. 1) [12]. The main fatty acid of tung oil is α -eleostearic acid (9-*cis*,11,13-*trans*-octadecatrienoic acid) (**2a**), which is an isomer of calendic acid and is the most commonly occurring conjugated triene fatty acid found, *e.g.*, in the oil of the tung oil tree (Fig. 1) [13]. Because of the chemical similarity to tung oil, which is already used as a drying oil for a number of products including varnishes, resins, inks, paints and coatings, calendula oil can be expected to show similar properties. Due to the highly reactive hexatriene system, calendic acid and α -eleostearic acid show an interesting reaction behavior [14]. Transesterification of calendula oil and tung oil is not trivial because reactions at the highly reactive hexatriene system have to be avoided. The conjugated double bonds in the oil as well as in the fatty acid esters are very sensitive to acids and oxygen, so that gentle reaction conditions are required.

The oxidation of drying oils such as tung oil and linseed oil, catalyzed by a cobalt catalyst, was studied by Oyman *et al.* [15]. The amount of oxygen taken up by linseed oil is significantly larger than that by tung oil, and the rate of the oxygen uptake is also higher. In linseed oil there is a strong build-up of peroxides (because of the double allylic methylene group), while in tung oil the build-up of hydroperoxides is much lower due to the direct radical addition to conjugated double bonds, consequently leading to the formation of a higher amount of cross-links and a lower amount of byproducts. In analogy, this also applies to calendula oil.

Tung oil is used, *e.g.*, in the production of a boat oil by the German company biopin [16]. The binding agent is cooked from linseed and tung oil and colophony. Citrus oil, a natural product, is used as solvent for processing. Citrus oil is a natural solvent; however, it evaporates as VOC like an ordinary petrochemical solvent. In other words, it would be a big step forward to substitute citrus oil by a non-volatile solvent. A good idea would be to have a reactive diluent participating in the cross-linking process.

Herein, we report on the development of an industrially feasible protocol for the transesterification of calendula oil and tung oil, and on studies of their properties as reactive diluents for alkyd resins.

2 Material and methods

2.1 Analytical equipment

Analytical GC was performed on a Carlo Erba GC series 4160 with an FID detector and a fused-silica capillary column DB1, 29 m. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker DRX 500 spectrometer at 20 °C, using TMS (^1H NMR) and CDCl_3 ($\delta = 77.0$ ppm, ^{13}C NMR) as internal standards. Mass spectra were recorded on a Finnigan MAT 95. All products were unambiguously identified by ^1H and ^{13}C NMR, and by MS (EI) or GC/MS (EI). The viscosity was measured using a RheoStress 6000 viscometer (Thermo Haake GmbH, Germany) or viscosity cups (4 and 6 mm). The pendulum hardness “König” was measured using an Elometer 3034 Pendulum Hardness Tester (TQC-Simex GmbH, Haan, Germany).

2.2 General

Calendula oil (59–65% calendic acid, 29% linoleic acid, 4% oleic acid, 4% palmitic acid) was obtained by extraction of the seeds of *Calendula officinalis*. Tung oil (84% α -eleostearic acid, 4% oleic acid, 4% linoleic acid, 2% palmitic acid) was purchased from biopin (Jever, Germany). Magnisol was obtained

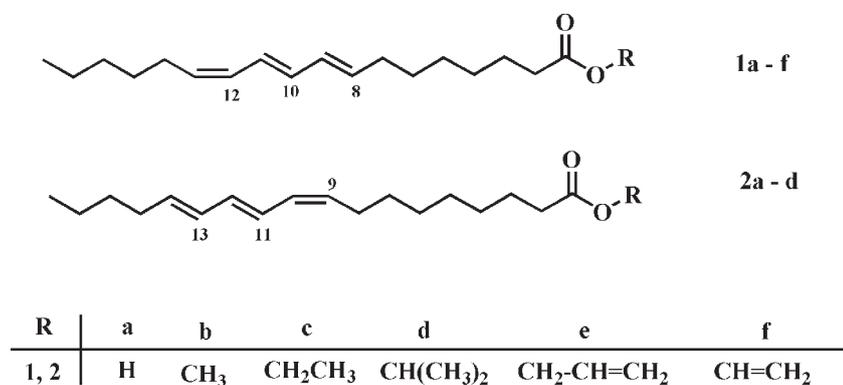


Figure 1. Calendic acid (8,10-*trans*,12-*cis*-octadecatrienoic acid) (**1a**) obtained from the seed oil of *Calendula officinalis* L. (Compositae) and α -eleostearic acid (9-*cis*,11,13-*trans*-octadecatrienoic acid) (**2a**) obtained from the oil of the nuts of the tung oil tree. The respective fatty acid esters were obtained by transesterification of calendula oil [methyl (**1b**), ethyl (**1c**), isopropyl (**1d**), allyl (**1e**) and vinyl calendulate (**1f**)] and tung oil [methyl (**2b**), ethyl (**2c**) and isopropyl α -eleostearate (**2d**)].

from the Dallas Group of America (Jeffersonville, USA), and hydrotalcit Syntal 701 HSAC from Süd-Chemie (München, Germany). Vinyl acetate and mercury acetate (Aldrich) were used without further purification.

Alkyd resins Worleekyd SO 8601 and Worleekyd L 7904 [17] as well as binders BM 2006 (highly viscous natural resin/oil binder) and BM 24 and desiccant (66% zirconium, 33% cobalt) (biopin) were used for hardening experiments with reactive diluents.

2.3 Transesterification of calendula oil and methanol using Syntal 701 HSAC

Calendula oil (10.0 g), methanol abs. (40 mL, 32 g, 1 mol) and hydrotalcit Syntal 701 HSAC (1 g) were stirred magnetically under reflux in a nitrogen atmosphere. The reaction was followed by thin-layer chromatography (TLC). After a reaction time of 48 h, the transesterification was quantitative. Hydrotalcit Syntal 701 HSAC was removed by filtration and methanol was removed *in vacuo*. Petroleum ether 60/80 (100 mL) was added and washed with H₂O (3 × 30 mL). The organic layer was dried with NaSO₄, filtered and the solvent evaporated. Yield 9.0 g, pale yellow oil; 59% of **1b** (GC).

2.4 Standard method for the transesterification of calendula oil and tung oil with alcohols such as methanol using sodium methoxide

Calendula oil or tung oil (10.0 g), methanol abs. (5 mL, 4.0 g, 125 mmol) and sodium methoxide (30% in methanol, 0.2 mL, 0.48 g, 0.9 mmol) were stirred magnetically in a nitrogen atmosphere at room temperature or alternatively at 60 °C. The reaction was followed by TLC. After a reaction time of 45 min (60 °C) or 2 h (room temperature), the transesterification was quantitative. The glycerol/methanol layer was separated and traces of solvent were removed *in vacuo*. After addition of petroleum ether 60/80 (20 mL) and Magnesol (0.5 g), the sample was stirred until the solution was neutral. The sample was filtered and the solvent evaporated.

2.5 Methyl 8,10-*trans*,12-*cis*-octadecatrienoate (**1b**)

1b was synthesized by the standard transesterification method. Yield 9.3 g, pale yellow oil. The product was obtained as a mixture of **1b** (65%), of methyl esters of linoleic acid (27%), oleic acid (2%) and palmitic acid (2%) as determined by GC; ¹H and ¹³C NMR data of **1b** that could be assigned unambiguously are given.

¹H NMR (500.1 MHz, CDCl₃): δ = 6.38 (dd, *J* = 14.3, 11.5 Hz, 1 H, H-9), 5.98 (dd, *J* = 11.0, 11.0 Hz, 1 H, H-12), 5.67 (dt, *J* = 14.3, 7.0 Hz, 1 H, H-8), 5.36 (m, 3 H, H-10, H-11, H-13), 3.65 (s, 3 H, OCH₃), 2.29 (t, *J* = 7.5 Hz, 2 H, H-2), 2.17 (ddt, *J* = 7.3, 1.3, 7.5 Hz, 2 H, H-14), 2.05 (dt, *J* = 7.0, 7.0 Hz, 2 H, H-7), 1.62 (m, 2H, H-3), 1.42–1.23 (m, 12H), 0.89 (t, *J* = 7.1 Hz, 3 H). ¹³C NMR (125.7 MHz,

CDCl₃): δ = 174.2, 134.8, 130.9, 130.7, 130.4, 128.6, 126.1, 51.4, 34.1, 32.7, 31.529.8–29.0 (5), 28.8, 25.6, 24.9, 13.9 ppm. GC-MS (EI): *m/z* (%) = 292 (68), 261 (7), 93 (92), 79(96), 67 (80), 40 (100).

2.6 Ethyl 8,10-*trans*,12-*cis*-octadecatrienoate (**1c**)

1c was synthesized by the standard transesterification method with ethanol abs. (5 mL, 3.9 g, 85 mmol). Yield 9.1 g, pale yellow oil; 59% of **1c** (GC).

Only NMR data that refer to the ethyl ester functionality are given. ¹H NMR (500.1 MHz, CDCl₃): δ = 4.11 (q, *J* = 7.1 Hz, 2 H, OCH₂CH₃), 1.25 (t, *J* = 7.1 Hz, 3 H, OCH₂CH₃). ¹³C NMR (125.8 MHz, CDCl₃): δ = 173.8, 60.1, 14.0 ppm.

2.7 Isopropyl 8,10-*trans*,12-*cis*-octadecatrienoate (**1d**)

1d was synthesized by the standard transesterification method with isopropanol (5 mL, 3.9 g, 65 mmol). Yield 8.7 g, pale yellow oil; 59% of **1d** (GC).

Only NMR data that refer to the isopropyl ester functionality are given. ¹H NMR (500.1 MHz, CDCl₃): δ = 5.0 (2 × q, *J* = 6.5 Hz, 1 H, CH(CH₃)₂), 1.21 (d, *J* = 6.5 Hz, 6 H, CH(CH₃)₂). ¹³C NMR (125.8 MHz, CDCl₃): δ = 173.3, 67.3, 21.8 (2 × CH₃). GC-MS (EI): *m/z* (%) = 320 (67), 277 (100), 261 (34), 93 (68), 79(64), 67 (41), 43 (52).

2.8 Allyl 8,10-*trans*,12-*cis*-octadecatrienoate (**1e**)

1e was synthesized by the standard transesterification method with allyl alcohol (5 mL, 4.3 g, 74 mmol). Yield: 8.2 g, pale yellow oil; 46% of **1e** (GC).

Only NMR data that refer to the allyl ester functionality are given. ¹H NMR (500.1 MHz, CDCl₃): δ = 5.90 (ddt, *J* = 17.3, 11.8, 5.5 Hz, 1 H, OCH₂CH=CH₂), 5.30 (d, *J* = 17.3 Hz, 1 H, OCH₂CH=CH₂), 5.21 (d, *J* = 11.8 Hz, 1 H, OCH₂CH=CH₂), 4.57 (d, *J* = 7.0 Hz, 2 H, OCH₂CH=CH₂). ¹³C NMR (125.7 MHz, CDCl₃): δ = 173.3, 132.3, 117.9, 64.8 ppm. MS (EI): *m/z* (%) = 318 (70), 277 (28), 93 (94), 91 (100).

2.9 Vinyl 8,10-*trans*,12-*cis*-octadecatrienoate (**1f**)

Calendic acid (**1a**) was used as starting material for the synthesis of **1f** and was prepared by saponification of calendula oil as described in the literature [18].

A mixture of **1a** (9 g, 32.4 mmol), vinyl acetate (17.2 g, 200 mmol) and mercury acetate (0.2 g, 0.63 mmol) was stirred magnetically in an inert atmosphere. After dropwise addition of H₂SO₄ (96–98%, 0.013 mL), the sample was heated under reflux for 2 h. The reaction was followed by TLC (petroleum ether/ether 8 : 2). Then, sodium acetate trihydrate (70 mg, 0.51 mmol) was added and the sample was

stirred magnetically overnight at room temperature. Unreacted vinyl acetate was removed *in vacuo* and the product was isolated by column chromatography (silica gel 60, petroleum ether/ether 8 : 2). Yield: 6.8 g, pale yellow oil, 42% of **1f** (GC).

NMR data that refer to the vinyl ester functionality are given. ^1H NMR (500.1 MHz, CDCl_3): $\delta = 7.29$ (dd, $J = 14.6, 7.2$ Hz, 1 H, $\text{CH}=\text{CH}_2$), 4.87 (d, $J = 14.6$ Hz, 1 H, $\text{CH}=\text{CH}_{\text{a(b)}}$), 4.55 (d, $J = 7.2$ Hz, 1 H, $\text{CH}=\text{CH}_{\text{a(b)}}$). ^{13}C NMR (125.7 MHz, CDCl_3): $\delta = 170.7, 141.2, 97.3$ ppm.

2.10 Methyl 9-cis,11,13-trans-octadecatrienoate (2b)

2b was synthesized by the standard transesterification method. Yield 8.9 g, pale yellow oil; 77% of **2b** (GC). ^1H and ^{13}C NMR data of **2b** that could be assigned unambiguously are given.

^1H NMR (500.1 MHz, CDCl_3): $\delta = 6.47$ (dd, $J = 14.1, 11.4$ Hz, 1 H, H-13), 6.12 ($2 \times$ dd, $J = 14.1, 11.0$ Hz, 2 H, H-11, H-12), 5.98 (dd, $J = 11.0, 11.0$ Hz, 1 H, H-10), 5.68 (dt, $J = 14.2, 7.1$ Hz, 1 H, H-14), 5.37 (dt, $J = 11.0, 7.7$ Hz, 1 H, H-9), 3.63 (s, 3 H, OCH_3), 2.29 (t, $J = 7.5$ Hz, 2 H, H-2), 2.16 (ddt, $J = 7.7, 1.3, 6.9$ Hz, 1 H, H-8), 2.09 (dt, $J = 7.1, 7.4$ Hz, 2 H, H-15), 1.61 (tt, $J = 7.3, 7.3$ Hz, 2 H, H-3), 1.41–1.31 (m, 12 H), 0.89 (t, $J = 6.7$ Hz, 3 H, H-18). ^{13}C NMR (125.8 MHz, CDCl_3): $\delta = 173.8, 135.1, 132.8, 130.6, 128.7, 125.9, 51.3, 34.0, 32.4, 30.3, 30.4, 29.7, 29.3, 29.0, 29.0, 27.3, 24.9, 22.2, 13.8$ ppm. GC-MS (EI): m/z (%) = 292 (100), 261 (17), 93 (96), 79(85), 67 (47), 41 (34).

2.11 Ethyl 9-cis,11,13-trans-octadecatrienoate (2c)

A mixture of tung oil (100 g), ethanol abs. (50 mL, 39 g, 850 mmol) and sodium methoxide (30%, 2 mL, 4.8 g, 9 mmol) was stirred magnetically and heated under reflux in a nitrogen atmosphere. The reaction was followed by TLC. After a reaction time of 15 min, the transesterification was quantitative. Then, the glycerol/ethanol layer was separated and traces of solvent were removed *in vacuo*. After addition of petroleum ether 60/80 (300 mL) and Magnesol (10 g), the sample was stirred until the solution was neutral (1 h). Then, the sample was filtered and the solvent evaporated. Yield: 94 g, pale yellow oil; 79% of **2c** (GC).

NMR data that refer to the ethyl ester functionality are given. ^1H NMR (500.1 MHz, CDCl_3): $\delta = 4.11$ (q, $J = 7.1$ Hz, 2 H, OCH_2CH_3), 1.25 (t, $J = 7.1$ Hz, 3 H, OCH_2CH_3). ^{13}C NMR (125.8 MHz, CDCl_3): $\delta = 173.8, 60.1, 14.0$ ppm.

Analogously, 500 g tung oil was reacted with 250 mL ethanol and 10 mL sodium methoxide (30%). After a reaction time of 30 min, the transesterification was quantitative. Petroleum ether 60/80 (1000 mL) and Magnesol (10 g) were added and the sample was stirred until the solution was neutral (1 h). Yield: 483 g.

2.12 Isopropyl 9-cis,11,13-trans-octadecatrienoate (2d)

2d was prepared in analogy to ester **2c** with isopropanol abs. (70 mL, 55 g, 908 mmol). Excess isopropanol was removed *in vacuo*. After addition of petroleum ether 60/80 (200 mL), glycerol was separated. The solvent was evaporated *in vacuo*. Yield: 71 g, pale yellow oil; 72% of **2d** (GC).

NMR data that refer to the ethyl ester functionality are given. ^1H NMR (500.1 MHz, CDCl_3): $\delta = 5.0$ ($2 \times$ q, $J = 6.5$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, $J = 6.5$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$) ppm. ^{13}C NMR (125.8 MHz, CDCl_3): $\delta = 173.3, 67.3, 21.8$ ($2 \times \text{CH}_3$). GC-MS (EI): m/z (%) = 320 (73), 277 (100), 261 (38), 93 (70), 79(65), 67 (43), 43 (53).

2.13 Alkyd resin: Typical formulation used by biopin

Standard alkyds contain an amount of oil of about 66%. Typical composition: linoleic acid (63%), pentaerythrol (13%) and phthalic anhydride (24%). The compounds are heated under reflux in xylene (16%) at 180–240 °C to keep the acid number below 10. The reaction takes 22 h, cooling down included. Small amounts of xylene remain in the resin.

2.14 Binder (VP 2431, BM 2030): Typical formulation used by biopin

The standard binder is prepared from tung oil (66.7%) and modified Chinese tree gum. After melting down of the gum to the oil at 170 °C, the temperature is raised to 220 °C. When the defined viscosity is achieved, the reaction mixture is cooled. The whole procedure takes 6–10 h.

2.15 White top coating: Typical formulation used by biopin

Components: BM 2051 (59.8%, binder with a 66% amount of oil), Shellsol D 40 (20.9%), white pigment paste (17.9%), drier (1.4%).

2.16 Outdoor and artificial weathering

Outdoor weathering was carried out using the standard binder on the basis of tung oil compared to a binder that was prepared on the basis of calendula oil by the described procedure used by biopin. The binders were applied to planks that were exposed at first for 6 months and then for another 6 months. In parallel, test patterns were checked by artificial weathering measurements for 3 weeks, which is comparable to a standardized outdoor weathering of 3 years.

3 Results and discussion

We studied different heterogeneous and homogeneous catalysts for the transesterification of calendula oil and tung oil, to obtain the respective esters containing as main component **1b–f** and **2b–d**, respectively (Fig. 1). Calendula oils with a content of calendic acid in the range of 59–65% were used. Furthermore, the oils contained linoleic, oleic, stearic, and palmitic acid. Using the conventional transesterification method with sodium or potassium hydroxide, only minor conversion of calendula oil was observed.

A basic hydrotalcit (Syntal 701 HSAC, Süd-Chemie) as heterogeneous catalyst gave methyl calendulate (**1b**) in good yield from the transesterification of calendula oil with methanol; however, the reaction time of 48 h to obtain full conversion was relatively long and, moreover, this hydrotalcit is not commercially available at present.

The homogeneous basic transesterification was carried out with catalysts such as sodium and potassium methoxide and potassium tert.-butylate. Best results using alcohols such as methanol and ethanol concerning the yields of the respective esters as well as the reaction procedure were obtained with sodium methoxide as catalyst.

Calendula oil, the catalyst and methanol were stirred in a nitrogen atmosphere for 2 h at room temperature, or alternatively for 45 min at 60 °C, to give methyl calendulate (**1b**) in quantitative yield (Fig. 2). The work-up was carried out with Magnesol (magnesium silicate), which is a solid acid and can easily be removed by filtration. Using Magnesol, the work-up was very much simplified because it was not necessary to wash and dry the organic layer as in conventional procedures.

All of the fatty acids in the triacylglycerol were converted into methyl esters, which were separated by GC and identified by GC/MS. The unambiguous characterization of **1b** was confirmed by ¹H and ¹³C NMR. The transesterification proceeded with retention of the stereochemistry of the conjugated triene system. Furthermore, calendula oil was transesterified with ethanol and isopropyl alcohol by this standard method, to give **1c** and **1d** in quantitative yields. Esters **1c** and **1d** (Fig. 1) were characterized as described for methyl calendulate (**1b**). The change of the ester functionality did not cause any change

in the NMR shifts of the signals belonging to the carbon and hydrogen atoms of the alkyl chains.

In analogy to calendula oil, tung oil was transesterified with methanol, ethanol, and isopropanol, catalyzed by sodium methoxide, to give the respective esters (Fig. 1). The characterization of esters **2b–2d** was carried out by GC, GC/MS, ¹H and ¹³C NMR, clearly indicating that the transesterification using sodium methoxide as catalyst proceeded with retention of the stereochemistry of the conjugated triene system.

Calendic acid esters **1b**, **1c**, and **1d** were tested as reactive diluents for binding agents. **1b** was applied to a highly viscous natural resin/oil binder (VP 2431), showing that the viscosity could be significantly decreased by a factor of 20 using the ester in an amount of 50% (Table 1). With this dilution, a workable binding agent that was easy to spread was obtained.

Table 1. Influence of methyl calendulate (**1b**) used as reactive diluent on the viscosity of binder VP 2431¹ (natural resin/oil binder).

	VP 2431 ¹	+ 1b (10%)	+ 1b (25%)	+ 1b (50%)
Viscosity [Pa s]	21.68	10.0	3.27	1.08

Furthermore, ester **1b** was applied as reactive diluent to the varnish binder BM 24, which was prepared on the basis of safflor fatty acid ester. The results show that methyl calendulate (**1b**) can be used to relevantly decrease the viscosity of the binder, depending on the amount of added **1b** (Table 2). In addition, good results were obtained for drying properties and pendulum hardness. However, an unfavorable side effect that was observed in the samples containing **1b** was a slight tackiness of the films.

Esters **1c** and **1d** were tested as reactive diluents for the binder BM 2030, which is used for coatings for interior and exterior applications. The coating was produced with Colinoleate as drier and small amounts of Shellsol D60 as cosolvent. A general abdication of the petrochemical solvent was not possible. Ethyl (**1c**) and isopropyl calendulate (**1d**) showed good properties as reactive diluent (Table 3). The resulting dilutions (samples B and C) were characterized by their low viscosity and good drying properties. Surprisingly,

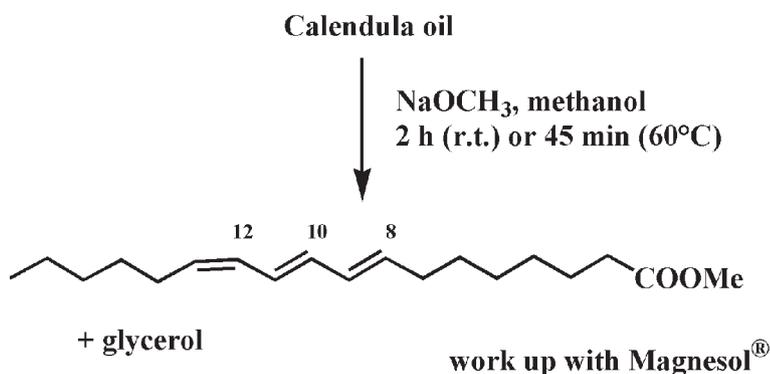


Figure 2. Transesterification of calendula oil with methanol in the presence of sodium methoxide as catalyst to give methyl calendulate (**1b**).

Table 2. Methyl calendulate (**1b**) used as reactive diluent for the varnish binder BM 24.

	BM 24 [§]					
	-	+ 10% 1b	+ 35% 1b	+ 50% 1b	+ 20% D60 [#]	+ 10% 1b + 10% D60
Solid body	100%	100%	100%	100%	80%	90%
Viscosity at 20 °C/viscosity cup 4 mm [§] [s]	no flowability	155	65	33	180	105
Viscosity at 20 °C/viscosity cup 6 mm [s]	180	42	20	12	45	34
Drying at 38 µm wet film thickness [h]	6–10	3	3–4	4–5	2–3	3
Pendulum hardness (König), after 3 days [s]	18	38	34	25	17	28

[§] BM 24 is a varnish binder that is based on safflor fatty acid ester and desiccated with 0.8% Co-linoleate (10%).

[§] The viscosity was measured according to DIN 53211 or EN ISO 2431, respectively.

[#] White spirit Shellsol D60 was used as cosolvent.

Table 3. Ethyl (**1c**) and isopropyl calendulate (**1d**) as reactive diluents for binder BM 2030.

	Sample		
	A	B	C
Solid body	74.5%	77.8%	77.8%
Viscosity [Pa s]	0.9	0.45	0.52
Drying at 38 µm wet film thickness [h]	5	3	3.5
Pendulum hardness (König), after 7 days [s]	55	17	17

Sample A: BM 2030 + Co-drier (0.75%) + Shellsol D40 (25%).

Sample B: Sample A + ethyl calendulate **1c** (15%).

Sample C: Sample A + isopropyl calendulate **1d** (15%).

they showed a shortening of the drying time of about 35–40% compared to the conventional sample A. However, in all tests, the pendulum hardness was not fully satisfactory. The film seemed to plasticize although it was plane and not at all tacky.

Furthermore ethyl (**1c**) and isopropyl calendulate (**1d**) were used as reactive diluents in a white top coating. Samples were exposed to artificial weathering and compared to samples that were stored at indoor temperature. The weathered samples kept the white color and showed a good curing. The properties were comparable to coatings typically prepared with Shellsol D40 as solvent. The cured coatings were extracted and analyzed with respect to monomeric fatty esters. Calendic acid esters **1c** and **1d** could not be detected by GC, giving clear evidence that they were incorporated completely into the film while curing. In contrast, the respective esters of linoleic acid, oleic acid, stearic acid, and palmitic acid being present as minor components were clearly detected.

Esters **2b–2d** were tested as reactive diluents in alkyd resin formulations in analogy to the respective esters of calendic acid **1b–1d**. The results were comparable, showing good properties as reactive diluents characterized by low viscosity

and good curing properties. Unfortunately, also esters **2b–2d** did not give better results concerning the pendulum hardness compared to the respective calendula esters.

We had thought that the application of allyl calendulate (**1e**) and vinyl calendulate (**1f**) (Fig. 1) as reactive diluent would give higher cross-linking in the cured films, due to the additional double bond. Ester **1e** was synthesized by transesterification of calendula oil with allyl alcohol, using our standard method. The synthesis of **1f** was not possible in this way. To obtain ester **1f**, calendic acid (**1a**), which was prepared by saponification of calendula oil, was reacted with vinyl acetate in the presence of mercury acetate and H₂SO₄ as catalyst, as described in the literature [19]. Both esters **1e** and **1f** were clearly characterized by GC/MS, ¹H and ¹³C NMR.

Contrary to our assumption, esters **1e** and **1f** did not show a better film formation compared to ethyl calendulate (**1c**). Therefore, further studies with **1e** and **1f** were not carried out, also with regard to the environmentally unacceptable catalyst that has to be used in case of the synthesis of **1f**.

4 Conclusions

Calendula oil obtained from a new oil crop that can be cultivated in Europe may be used comparably to tung oil in many coating applications. This opportunity provides new perspectives to the coating industry because the tung oil market is not stable. A gentle transesterification of calendula oil and tung oil with alcohols such as methanol, ethanol, and isopropanol in the presence of sodium methoxide as catalyst allows the synthesis of the respective esters, which can be used as reactive diluents for alkyd resins in coating applications. The reduction or even the substitution of organic solvents in the coating processing by reactive diluents derived from renewable material would be an important contribution to the necessary reduction of VOC.

Acknowledgments

We thank the “Deutsche Bundesstiftung Umwelt” for financial support of this work, Brian Cooke from the Dallas Group for providing Magnesol, and Dr. Uwe Flessner, Süd-Chemie AG, for the donation of Hydrotalcit.

Conflict of interest statement

The authors have declared no conflict of interest.

References

- [1] M. Eissen, J. O. Metzger, E. Schmidt, U. Schneidewind: 10 Years after Rio – Concepts on the contribution of chemistry to a sustainable development. *Angew Chem.* 2002, **114**, 402–425; *Angew Chem Int Ed.* 2002, **41**, 414–436.
- [2] J. Wolf, G. Manier, T. Eikmann, G. Scholl, G. Feldhaus, K. Grefen, P. Bruckmann, H. Pfeffer, K. Lütze, E. Schmidt, T. Schmidt, T. Pilhofer, H. Krill, H. Menig, S. Schirz, H. Pollack, W. Simmler: Air. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Online Edn. VCH, Weinheim (Germany) 2008.
- [3] F. N. Jones: Alkyd resins. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Online Edn. VCH, Weinheim (Germany) 2003.
- [4] U. Poth: Drying oils and related products. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Online Edn. VCH, Weinheim (Germany) 2001.
- [5] J. O. Metzger: Organic reactions without solvents and fats and oils as renewable raw materials for the chemical industry. *Chemosphere.* 2001, **43**, 83–87.
- [6] R. A. Hancock, N. J. Leeves, P. F. Nicks: The volatile by-products resulting from the autoxidation of unsaturated fatty acid methyl esters. *Prog Org Coat.* 1989, **17**, 321–336.
- [7] D. Stoye, W. Funke, L. Hoppe, J. Hasselkus, L. G. Curtis, K. Hoehne, H.-J. Zech, P. Heiling, M. Yamabe, K. Dören, H. Schupp, R. Küchenmeister, M. Schmitthenner, W. Kremer, W. Wiczor: Paints and coatings. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Online Edn. VCH, Weinheim (Germany) 2006.
- [8] T. Zonjee, DSM NV (NL): Patent EP0685543 (1995).
- [9] H. Meier zu Beerentrop, G. Röbbelen: *Calendula* and *Coriandrum* – New potential oil crops for industrial uses. *Fat Sci Technol.* 1987, **6**, 227–230.
- [10] CARMINA, Final Project Report, Executive Summary, <http://www.defra.gov.uk/farm/acu/research/reports/NF0503.pdf>.
- [11] <http://www.calendula-oil.com>.
- [12] R. J. Janssens, W. P. Vernooij: *Calendula officinalis*: A natural source for pharmaceutical, oleochemical, and functional compounds. *Inform.* 2001, **12**, 468–477.
- [13] F. D. Gunstone, J. L. Harwood: *The Lipid Handbook*. 2nd Edn. Academic Press, New York, NY (USA) 1994.
- [14] U. Biermann, W. Butte, T. Eren, D. Haase, J. O. Metzger: Diels–Alder reactions with conjugated triene fatty acid esters. *Eur J Org Chem.* 2007, 3859–3862.
- [15] Z. O. Oyman, W. Ming, R. van der Linde: Oxidation of drying oils containing non-conjugated and conjugated double bonds catalyzed by a cobal catalyst. *Prog Org Coat.* 2005, **54**, 198–204.
- [16] <http://www.biopin.de>.
- [17] <http://www.worlee.de>.
- [18] M. J. Chisholm, C. Y. Hopkins: Conjugated fatty acids of tragopogon and calendula seed oils. *Can J Chem.* 1960, **38**, 2500–2507.
- [19] D. Swern, E. F. Jordan Jr.: In: *Organic Synthesis Collective Volume IV*. Ed. N. Rabjohn, John Wiley & Sons Inc., New York (USA) 1963, p. 977.