New Route for Synthesis of Furan Derivatives from Protected α-Ketols and Ketones. A Total Synthesis of Furoventalene

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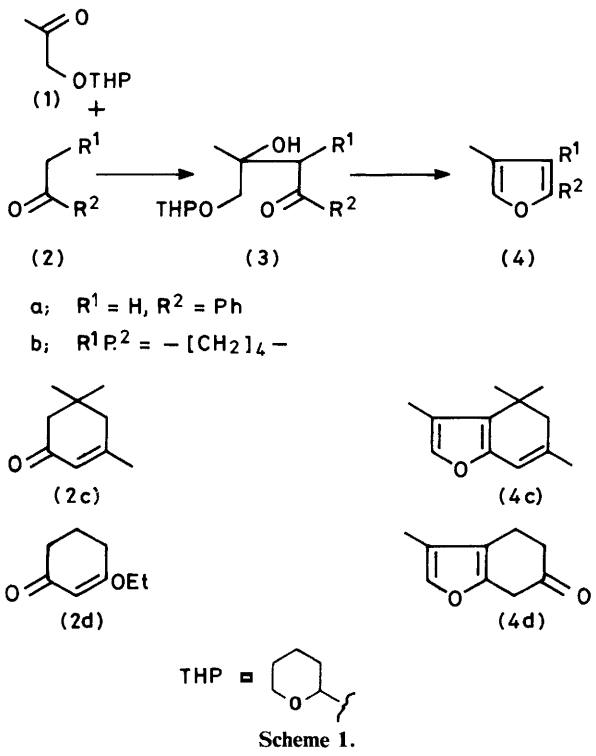
Reaction of acetonyl tetrahydropyranyl ether (1) with ketones (2a—d) in the presence of lithium diisopropylamide and zinc chloride produces the cross-aldol condensation products (3a—d), which are transformed into 3-methylfurans (4a—d), by treatment with aqueous toluene-*p*-sulphonic acid. Similarly, tetrahydrobenzofurans (7a—d) are obtained by using 2-hydroxycyclohexanone trimethylsilyl ether (5). The application of this methodology enabled us to complete a total synthesis of furoventalene (11).

Compounds having a furan moiety have been widely found in nature, especially in plants [1] and recently in marine organisms.[2] Despite the actual isolation of a number of natural substances, some derivatives lacking an electron-withdrawing group on a furan ring are known to be relatively unstable (*e.g.* synthetic DL-9,10-dehydrofuranoeremophilane was found to decompose within 1 h after isolation, even in a refrigerator).[3,4] In order to synthesize such unstable furan derivatives, it is desirable that the furan part should be constructed near the end of a synthetic sequence using readily available precursors and under mild conditions. Previously, we reported that, in the synthesis of several furanoeremophilane sesquiterpenes, elaboration of the furan moiety was achieved by acidic treatment of the products obtained from the zinc chloride-assisted cross-aldol condensation reaction of acetonyl tetrahydropyranyl ether (1) with the kinetically controlled enolates of conjugated octalone derivatives.[4] In this paper we provide further proof of the utility of this methodology for the preparation of various furan derivatives and an account of its application to the total synthesis of furoventalene (11).

First, in view of the abundance of fused 3-methylfuran derivatives in nature, acetonyl tetrahydropyranyl ether (1)[5] was employed as the protected α-ketol component. Compound (1) was easily prepared by the reaction of 1-hydroxyacetone with dihydropyran in methylene dichloride using pyridinium toluene-*p*-sulphonate (PPTS) as a catalyst.

A ketonic component (2) was treated with lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at −78 °C and then with compound (1) in the presence of zinc chloride. In this reaction, quenching the reaction below −30 °C by the addition of saturated aqueous ammonium chloride is essential in order to prevent a retro-aldol process. Upon treatment with toluene-*p*-sulphonic acid monohydrate (PTSA) in hot aqueous dioxane the cross-aldol condensation product (3) was obtained and, without purification, underwent simultaneous deprotection, cyclization, and dehydration to give the corresponding 3-methylfuran derivative (4) (Scheme 1). As seen from Table 1, the yields of the products were modest except for entry 1, and α,β-unsaturated ketones (entries 3 and 4) reacted with (1) as the kinetic enolate form under the conditions examined. In the case of 3-ethoxycyclohex-2-en-1-one (2d) (entry 4), hydrolysis of the enol ether function also took place during acid treatment to give the ketonic product (4d).

Next, readily available 2-hydroxycyclohexanone trimethylsilyl ether (5)[6] was employed as the representative cyclic α-ketol component. Under the same conditions, the reaction of (5) with ketone enolates also proceeded cleanly to produce the cross-aldol products (6), which in turn afforded, by treatment with PTSA, the tetrahydrobenzofuran derivatives (7) in satisfactory yield as depicted in Scheme 2 and Table 2. In the



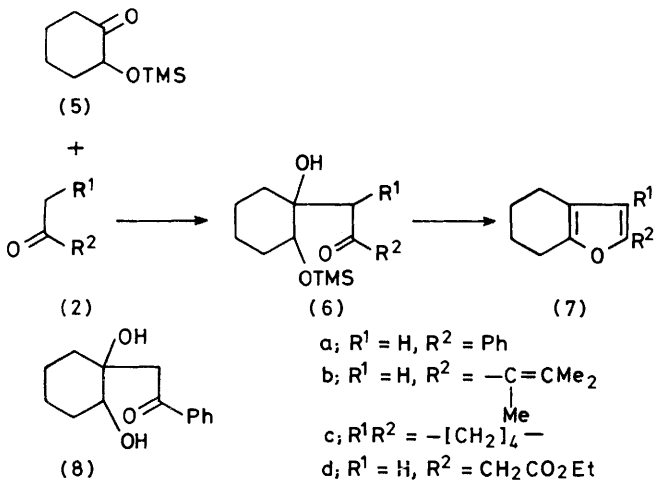
Scheme 1.

Table 1. Furans from acetonyl tetrahydropyranyl ether (1) and ketones

Entry	Ketone (2)	Product	Yield (%)
1	Acetophenone	(4a)	73 [a] (ref. 7)
2	Cyclohexanone	(4b)	40 [a] (ref. 8)
3	Isophorone	(4c)	50 [b]
4	3-Ethoxycyclohex-2-en-1-one	(4d)	37 [b]

[a] Yields are for the isolated pure products based on the amount of ketone consumed, and were not optimized. [b] Yields are for the isolated pure products based on the amount of aldol (3) consumed, and were not optimized.

reaction with acetophenone (entry 1), the dihydroxy ketone derivative (8) was isolated in addition to the furan (7a) (48%), in 43% yield. Compound (8) was found to be a single stereoisomer, but at present the stereochemistry has not been determined. Compound (8) could be converted into (7a) in



Scheme 2.

Table 2. Furans from 2-hydroxycyclohexanone trimethylsilyl ether (5) and ketones

Entry	Ketone (2)	Product	Yield [a] (%)
1	Acetophenone	(7a)	48 (ref. 9)
2	3-Isopropylbut-3-en-2-one	(7b)	56
3	Cyclohexanone	(7c)	76 (ref. 10)
4	Ethyl acetoacetate	(7d)	65

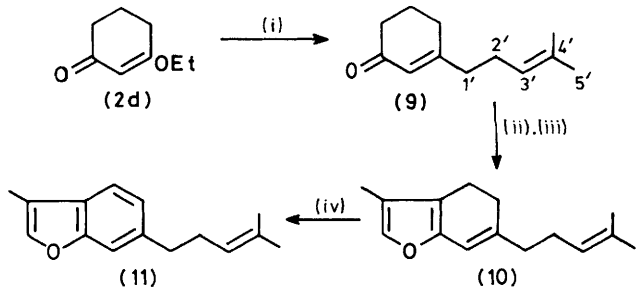
[a] Yields are for the isolated pure products based on the amount of ketone consumed, and were not optimized.

86% yield by treatment with (+)-camphorsulphonic acid in refluxing benzene using a Dean–Stark water separator. In the case of entry 2, migration of the double bond was observed during acid-catalysed ring closure. It should be noted that the dianion of ethyl acetoacetate [11] was also a good aldol addend (entry 4) and in this case the aldol condensation was found to proceed without the addition of zinc chloride.

As is clear from the examples cited above, the simplicity of the operation and the ready availability of both reactants, α-ketols [12] and ketones (aromatic ketones, cyclic ketones, α,β-unsaturated ketones, or β-keto esters) indicate that this procedure should be a convenient method for the synthesis of a variety of furan derivatives,[13] although the products are unstable.

Synthesis of Furoventalene.—Furoventalene (11) is an irregular sesquiterpenoid isolated from the sea fan *Gorgonia ventalis* [14] and contains a benzofuran system. Two syntheses have been reported so far, the one by Weinheimer and Washecheck [14] and the other by Yoshikoshi and his co-workers.[15] The former synthesis was achieved in a non-regioselective manner and the latter *via* a multi-step sequence through a highly oxygenated intermediate. The present method for the furan synthesis would provide an alternative approach to the synthesis of (11) in a regioselective and more straightforward manner.

Our synthetic scheme is illustrated in Scheme 3. In view of the instability and the low yield of (4d) (entry 4 in Table 1), one of the plausible precursors, it was decided first to prepare 3-(4-methylpent-3-enyl)cyclohex-2-en-1-one (9) from 3-ethoxycyclohex-2-en-1-one (2d). Compound (9) was easily prepared in 82% yield by the reaction of (2d) with 4-methylpent-3-enylmagnesium iodide and then by silica-gel chromatography. With the requisite compound (9) in hand, the application of the present method using acetonyl tetrahydropyranyl ether (1) was examined. In a similar fashion, the reaction of the enolate of (9) with (1) and the subsequent acid treatment afforded the known dihydrobenzofuran precursor (10) [15] in 69% yield. Dehydrogenation of (10) with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) furnished furoventalene (11) (32% yield), identical with an authentic sample.



Scheme 3. *Reagents:* (i) $Me_2C{=}CH(CH_2)_2MgI$–Et_2O; (ii) LDA–$ZnCl_2$–THF, then acetonyl tetrahydropyranyl ether; (iii) PTSA–dioxane–H_2O; (iv) DDQ–benzene

Experimental

I.r. spectra were recorded for solutions in carbon tetrachloride on a JASCO A-3 spectrophotometer. ^1H N.m.r. spectra were obtained for solutions in deuteriochloroform with a JEOL PMX-60 (60 MHz) instrument with tetramethylsilane as internal standard. Mass spectra were obtained on a JEOL JMS-DX 300 spectrometer. Microanalysis was carried out in the microanalytical laboratory of this Institute. Extractions with ether refer to the use of diethyl ether.

Acetonyl Tetrahydropyranyl Ether: Improved Procedure (1). —1-Hydroxyacetone was freshly distilled from commercially available 50% methanol solution at 70 °C at 10 mmHg pressure. A solution of the ketol (1.893 g, 25.6 mmol), dihydropyran (2.57 g, 30.7 mmol), and PPTS (64 mg, 0.26 mmol) in anhydrous methylene dichloride (9 ml) was stirred at room temperature for 22 h. After evaporation of the solvent under reduced pressure, anhydrous ether was added to precipitate PPTS which was then removed by filtration through neutral alumina. Evaporation of the filtrate, followed by distillation at 50—55 °C at 5 mmHg pressure, gave the tetrahydropyranyl ether (1) (3.426 g, 85%); δ 1.30—2.20 (6 H, m, $[CH_2]_3$), 2.17 (3 H, s, COMe), 3.25—4.17 (2 H, m, $OCHOCH_2[CH_2]_3$), 4.17 (2 H, br s, OCH_2COMe), and 4.65 (1 H, br s, $OCHO[CH_2]_4$).

General Procedure for Cross-aldol Reaction.—To a solution of LDA (1.2 mmol) in anhydrous THF (1 ml) and hexane (0.65 ml) was added dropwise a solution of a ketone (2) (1 mmol) in THF (1—2 ml), and the mixture was stirred at between −78 and −60 °C for 30 min under nitrogen. A solution of zinc chloride (0.5 mmol) in THF (1 ml) and then a solution of the protected α-ketol (1) or (5) (1.5 mmol) in THF (1 ml) were then added. The resulting reaction mixture was stirred at −60 °C for 30 min and quenched by aqueous ammonium chloride. The product was extracted with ether (2 × 50 ml). The combined extracts were washed in turn

with water and brine, dried, and evaporated to dryness. The residue was used, without purification, in the subsequent reaction.

General Procedure for Furan Synthesis.—The crude aldol (*ca.* 1 mmol) and PTSA (50 mg) were dissolved in aqueous dioxane (75%; 4 ml), and the resulting solution was heated at 70—80 °C for 1 h. Progress of the reaction was monitored by t.l.c. After the mixture had cooled to room temperature, the product was extracted with ether (2 × 50 ml). The combined extracts were washed in turn with water and brine. After evaporation of the solvent, the residue was purified by silica-gel t.l.c. or column chromatography to give the furan (4) or (7). The use of PPTS was unsatisfactory, resulting in decomposition.

4-*Methyl*-2-*phenylfuran* (4a). The reaction with acetophenone (2a) (226 mg, 2 mmol) was carried out in the same manner as described in the general procedure and gave the furan (4a) (231 mg, 73%); $\nu_{max.}$ 1 600, 1 450, 1 260, and 910 cm^{-1}; δ 2.03 (3 H, s, Me), 6.46 (1 H, s, 3-H), and 7.00—7.80 (6 H, m, Ph and 5-H) (Found: M^+, 158. $C_{11}H_{10}O$ requires *M*, 158).

4,5,6,7-*Tetrahydro*-3-*methylbenzofuran* (4b). The reaction with cyclohexanone (2b) (196 mg, 2 mmol) was carried out in the same manner as described in the general procedure and gave the furan (4b) (110 mg, 40%); $\nu_{max.}$ 1 645, 1 565, 1 445, 1 310, 1 270, 1 150, 1 100, 900, 730, and 610 cm^{-1}; δ 1.60—2.10 (4 H, m, 5- and 6-H_2), 1.92 (3 H, br s, Me), 2.20—2.80 (4 H, m, 4- and 7-H_2), and 6.98 (1 H, br s, 2-H) (Found: M^+, 136. $C_9H_{12}O$ requires *M*, 136).

4,5-*Dihydro*-3,4,4,6-*tetramethylbenzofuran* (4c). The aldol reaction of isophorone (2c) (278 mg, 2 mmol) was carried out in the same manner as described in the general procedure except for differences in reaction time (1.5 h) and temperature (−60 to −20 °C). Preparative t.l.c. [hexane–ethyl acetate (1 :5) as eluant] afforded the aldol (171 mg, 29%) and recovered isophorone (219 mg). The aldol (3c) (54 mg, 0.18 mmol) and a catalytic amount of PTSA were dissolved in aqueous THF (33%; 4 ml) and the resulting solution was heated at 60 °C for 20 min. Work-up in the usual manner gave the furan (4c) (16 mg, 50%). This furan decomposed completely on being kept at room temperature overnight; δ 1.18 (6 H, s, 4-Me_2), 1.87 (3 H, br s, 6-Me), 2.05 (3 H, br s, 3-Me), 2.00—2.20 (2 H, br s, 5-H_2), 6.07 (1 H, m, 7-H), and 6.90 (1 H, br s, 2-H).

4,5,6,7-*Tetrahydro*-3-*methyl*-6-*oxobenzofuran* (4d). The aldol reaction with 3-ethoxycyclohex-2-en-1-one (2d) (287 mg, 2 mmol) was carried out in the same manner as described in the general procedure and gave the aldol (3d) (452 mg, 74%) after preparative t.l.c. The aldol (103 mg, 0.35 mmol) and PTSA (29 mg, 0.15 mmol) were heated at 90 °C in benzene (2.5 ml) and H_2O (1 ml) overnight. Work-up in the usual manner gave the furan (4d) (19 mg, 37%). This furan decomposed completely on being kept at room temperature overnight; $\nu_{max.}$ 1 730, 1 310, 1 095, 915, and 730 cm^{-1}; δ 2.00 (3 H, br s, Me), 2.67 (4 H, br s, 4- and 5-H_2), 3.48 (2 H, br s, 7-H_2), and 7.13 (1 H, br s, 2-H).

4,5,6,7-*Tetrahydro*-2-*phenylbenzofuran* (7a). The reaction of acetophenone (2a) (120 mg, 1 mmol) and (5) was carried out in the same manner as described in the general procedure and gave the furan (7a) (90 mg, 48%) and the dihydroxy ketone (8) (108 mg, 43%). The benzofuran (7a) had $\nu_{max.}$ 1 600, 1 485, 1 440, and 1 300 cm^{-1}; δ 1.40—2.10 (4 H, m, 5- and 6-H_2), 2.10—2.90 (4 H, m, 4- and 7-H_2), 6.42 (1 H, s, 3-H), and 7.10—7.90 (5 H, m, Ph) (Found: M^+, 198. $C_{14}H_{14}O$ requires *M*, 198).

The dihydroxy ketone (8) had $\nu_{max.}$ 3 560, 3 480, 1 670, 1 450, and 1 210 cm^{-1}; δ 1.17—2.20 (8 H, m, 4 × CH_2), 3.10 (1 H, B part of AB q, *J* 17 Hz, C*H*HCOPh), 3.44 (1 H, A part of AB q, *J* 17 Hz, CH*H*COPh), 3.17—4.50 [3 H, br, CH(OH) and OH], and 7.25—8.20 (5 H, m, Ph). A solution of the dihydroxy ketone (8) (100 mg, 0.4 mmol) and (+)-camphor-10-sulphonic acid (15 mg, 0.06 mmol) in benzene (20 ml) was refluxed under a Dean–Stark water separator for 30 min. After being cooled to room temperature, the resulting solution was washed in turn with water and brine. Evaporation of the solvent followed by preparative t.l.c. [hexane–ethyl acetate (1 :3) as eluant] gave the furan (7a) (64 mg, 86%).

4,5,6,7-*Tetrahydro*-2-(1,2-*dimethylprop*-1-*enyl*)*benzofuran* (7b). The aldol reaction of 3-isopropylbut-3-en-2-one (80 mg, 0.7 mmol) was carried out in the same manner as described in the general procedure. After heating the crude aldol in the same manner as described in the general procedure, benzene (40 ml) was added and the resulting solution was heated under a Dean–Stark water separator for 1 h. Work-up in the usual manner gave the benzofuran (7b) (76 mg, 56%); $\nu_{max.}$ 1 440, 1 225, 1 130, 915 and 730 cm^{-1}; δ 1.50—2.10 (4 H, m, 5- and 6-H_2), 1.81 (3 H, s, Me), 1.93 (6 H, s, 2 × Me), 2.10—2.80 (4 H, m, 4- and 7-H_2), and 5.93 (1 H, s, 3-H) (Found: $M^+ + 1$, 191. [$C_{13}H_{19}O$] requires *m*/*z*, 191).

1,2,3,4,6,7,8,9-*Octahydrodibenzofuran* (7c). The reaction of cyclohexanone (98 mg, 1 mmol) with (5) was carried out in the same manner as described in the general procedure and gave the benzofuran (7c) (133 mg, 76%); $\nu_{max.}$ 1 450, 1 365, 1 300, 1 270, 1 240, 1 150, 1 130, and 900 cm^{-1}; δ 1.17—2.10 (8 H, m) and 2.10—2.83 (8 H, m).

Ethyl 4,5,6,7-*tetrahydrobenzofuran*-2-*ylacetate* (7d). To a stirred suspension of sodium hydride (23 mg, 0.96 mmol) in THF (1 ml) in an ice-bath, and under nitrogen, was added ethyl acetoacetate (108 μl, 0.85 mmol) and the mixture was stirred for 10 min. A solution of n-butyl-lithium (0.85 mmol) in hexane (0.5 ml) was then added and the mixture was stirred for 10 min at an ice-bath temperature. A solution of 2-hydroxycyclohexanone trimethylsilyl ether (5) (167 mg, 0.93 mmol) in THF (1.5 ml) was added to the above dianion solution, and the resulting mixture was stirred at an ice-bath temperature and worked up as usual. Evaporation of the solvent left the aldol (6d) (272 mg), which was used without purification. The crude aldol was dissolved in 33% aqueous dioxane (4 ml) with PTSA (26 mg) and heated at 90 °C for 30 min. Benzene (30 ml) was added to the solution, and the resulting mixture was heated under reflux using a Dean–Stark water separator for 1 h. Work-up in the usual manner afforded the ester (7d) (114 mg, 65%); $\nu_{max.}$ 1 740, 1 250, 1 220, 1 160, 1 040, and 975 cm^{-1}; δ 1.25 (3 H, t, *J* 7 Hz, CH_2*Me*), 1.50—2.00 (4 H, m, 5- and 6-H_2), 2.10—2.70 (4 H, m, 4- and 7-H_2), 3.58 (2 H, s, CH_2CO_2Et), 4.19 (2 H, q, *J* 7 Hz, CH_2Me), and 6.00 (1 H, s, 3-H); *m*/*z* 135 ($M^+ - CO_2Et$).

3-(4-*Methylpent*-3-*enyl*)*cyclohex*-2-*en*-1-*one* (9).—To a stirred mixture of magnesium (121 mg, 5 mmol) in anhydrous diethyl ether (2 ml) under nitrogen was added dropwise a solution of 4-methylpent-3-enyl iodide (1.057g, 5 mmol) in diethyl ether (7 ml). The resulting mixture was refluxed gently for 1 h and cooled with an ice-bath. A solution of 3-ethoxycyclohex-2-en-1-one (2d) in diethyl ether (6 ml) was added at that temperature, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by the addition of aqueous ammonium chloride, and the product was extracted with ether. Evaporation of the ether and preparative t.l.c. [silica gel; eluant diethyl ether–light petroleum b.p. 30—50 °C (1 : 4)] of the residue afforded the *dienone* (9) (436 mg, 82%) and recovered starting material (2d) (96 mg, 23%). An analytical sample of (9) was obtained by distillation (70—80 °C at 0.25 mmHg); $\nu_{max.}$ 1 670, 1 615, 1 370, 1 340, 1 320, 1 250, and 1 190 cm^{-1}; δ 1.62 (3 H, s, Me), 1.70 (3 H, s, Me), 1.80—2.60 (10 H, m, 5 × CH_2), 5.08 (1 H, m, 3′-H), and

5.87 (1 H, br s, 2-H) (Found: C, 80.7; H, 10.4. $C_{12}H_{18}O$ requires C, 80.9; H, 10.2%).

4,5-Dihydro-3-methyl-6-(4-methylpent-3-enyl)benzofuran (10).—To a stirred solution of LDA, prepared from di-isopropylamine (147 μl, 1.05 mmol) and n-butyl-lithium (0.87 mmol) in diethyl ether (1 ml) and hexane (0.58 ml), was added a solution of the dienone (9) (130 mg, 0.73 mmol) in diethyl ether (5 ml) at −68 °C under nitrogen. After the mixture had been stirred for 30 min, a solution of zinc chloride (51 mg, 0.37 mmol) in diethyl ether (2.5 ml) and then a solution of acetonyl tetrahydropyranyl ether (1) (190 mg, 1.20 mmol) in diethyl ether (2.5 ml) were added. The resulting mixture was stirred for 1.4 h and quenched at −30 °C with aqueous ammonium chloride. The product was extracted with ether, and the combined extracts were washed in turn with water and brine. Evaporation of the ether left the crude aldol (343 mg), which was used for the subsequent reaction without purification.

The crude aldol (343 mg) and PTSA (15 mg) were dissolved in 25% aqueous THF (5 ml), and the resulting solution was heated at 70 °C for 1.25 h. After the mixture had cooled to room temperature, the product was taken up in diethyl ether (2 × 50 ml), and the combined ether layers were washed in turn with water and brine. Evaporation of the ether followed by preparative t.l.c. [silica gel; eluant diethyl ether–light petroleum b.p. 30—50 °C (1 : 9)] afforded the dihydrobenzofuran (10) [108 mg, 69% from enone (9)]. *Ca.* half of the benzofuran (10) decomposed after being kept overnight in a freezer.

Furoventalene (11).—To a stirred solution of DDQ (97%; 32 mg, 0.14 mmol) in anhydrous benzene (1 ml) was added a solution of the freshly prepared dihydrobenzofuran (10) (25 mg, 0.12 mmol) in benzene (4 ml). The solution changed its colour from brown to deep green upon the addition of (10). After being stirred at room temperature for 10 min, the resulting solution was passed through a short column of a silica gel with the aid of light petroleum. Evaporation of the solvents left furoventalene (11) (8 mg, 32.3%). The ^1H n.m.r. (100 MHz) and i.r. spectra were completely identical with those of an authentic sample.

Acknowledgements

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