Stereoselective hydrogenation of (R)-$(+)$-pulegone and $(2S,5R)$-$(-)$-menthone in presence of β-cyclodextrin and its derivatives

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Abstract

Stereoselective hydrogenation of (R)-$(+)$-pulegone and $(2S,5R)$-$(-)$-menthone over Raney nickel at room temperature with dilute and concentrated alkali in presence of β-cyclodextrin and its derivatives was studied. The effect of alkali and β-cyclodextrin and its derivatives on the modification of the yield and the proportion of epimeric alcohols formed were found to be the salient features of this reaction (Scheme 1). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; (R)-$(+)$-pulegone; $(2S,5R)$-$(-)$-menthone; β-cyclodextrin

(R)-$(+)$-pulegone and $(2S,5R)$-$(-)$-menthone are widely distributed in the plant kingdom [1,2]. Pulegone is found most abundantly (about 96.9%) in the plant of *Acinos svavedens* [3]. Essential oil from *Mentha piperita* contains high enantiomeric purity (90–100%) of (R)-$(+)$-pulegone [4]. Pulegone is present to the extent of about 80% in Pennyroyal oil obtained by steam distillation of the flowering tops of *Mentha pulegium* [5]. Pulegone is also a major constituent of essential oils from other plant materials like *Mentha arvensis* [6] and *Mentha sylvestis* [7]. Menthone also occurs in nature and is widely distributed in the plant kingdom. It is present in high concentrations in few Mentha species like *Mentha spicata aromentha* 80%, Buchu leaf 40% [8] and *M. arvensis* 26% [2]. It is also present to the extent of 35 to 74% in the essential oils of peppermint, geranium and other mint oils [9]. Reduction of these oils enriched with menthone and pulegone using various catalysts and conditions results in the formation of mixture of menthones and menthols [10–12]. In menthol alone eight optically active isomers are possible. Reduction of pulegone or menthone or their essential oil sources with improved selectivity would be of practical importance, especially in the production of menthol.

The commonly applied reducing systems for the reduction of menthone and pulegone are sodium dithionite [13], sodium borohydride [14],

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Scheme 1.
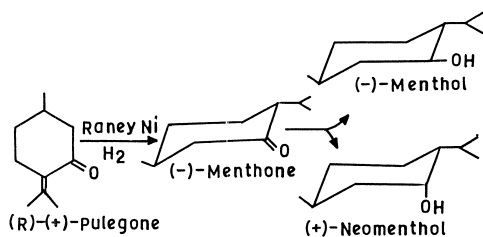
and Rh on silica or alumina [15]. Reduction by hydrogenation of pulegone and menthone could also be accomplished under mild conditions, using Raney Ni. Raney Ni has been extensively

used as a hydrogenation catalyst for the reduction of olefinic and carbonyl groups. Hydrogenation of *Minthostachys verticillata* essential oil yielded menthone, menthol and neomenthol depending on the presence and absence of alkali [16].

Among other procedures, the reaction in presence of β-cyclodextrin often results in the alteration of well known chemical transformations [17]. Earlier β-cyclodextrin (β-CD) and its derivatives have been shown to effectively alter the product distribution of reduction products of menthone and pulegone with various reducing

Table 1
Effect of β-CD and alkali on hydrogenation of pulegone over Raney Ni[a]

NaOH in ml	Catalyst in molar equivalents of ketone	Menthone + Isomenthone	Neo-menthol	Neoiso-menthol	Menthol	Total	Menthol/ Neomenthol	Pulegone	Unknown
Without alkali									
	Control[b]	92.6	0.8	0.0	2.6	3.4	3.3	1.7	2.3
	β-CD (1.0)	69.9	2.6	0.0	23.3	25.9	9.0	0.0	4.2
	β-CD-polymer (1.0)	78.0	2.1	0.0	4.4	6.5	2.1	0.0	15.5
	DMβ-CD (0.5)	98.0	0.0	0.0	1.9	1.9	–	0.0	0.1
	CTAB (1.0)	96.0	1.3	0.0	2.1	3.4	1.6	0.0	0.6
With 40% alkali									
0.5	Control[b]	22.4	24.5	0.0	52.3	76.8	2.1	0.0	0.8
0.5	β-CD (1.0)	9.9	30.0	0.0	59.8	89.8	1.0	0.0	0.3
0.5	β-CD-polymer (1.0)	23.9	28.6	0.0	28.9	57.5	1.0	0.0	18.6
0.5	DMβ-CD (0.5)	54.9	14.8	0.0	29.7	44.5	2.0	0.0	0.6
0.5	CTAB (1.0)	47.0	15.2	0.0	22.8	38.0	1.5	0.0	15.0
With 10% alkali									
0.3	–	44.1	12.9	24.4	4.9	42.2	0.4	5.1	8.6
0.9	–	86.6	3.2	4.4	0.5	8.1	0.2	0.3	0.5
1.4		91.8	0.6	0.5	0.2	1.3	0.3	0.6	6.3
1.8	–	96.3	0.6	0.0	0.3	0.9	0.5	0.0	2.8
0.3	β-CD (0.1)	1.6	40.8	42.5	12.1	95.4	0.4	1.0	2.1
0.6	0.1	3.3	38.7	39.8	11.2	87.7	0.3	1.6	5.4
0.9	0.1	28.0	24.7	37.6	6.2	68.5	0.3	0.7	2.8
1.2	0.1	76.8	7.5	11.5	1.6	19.0	0.3	0.4	2.7
1.5	0.1	77.0	7.4	11.5	1.5	18.9	0.2	0.3	3.8
1.8	0.1	55.1	12.8	21.0	5.8	39.6	0.5	0.9	4.4
0.3	0.5	62.1	12.5	21.8	3.5	37.8	0.3	0.0	0.1
0.3	0.7	67.3	10.0	16.9	2.9	29.8	0.3	0.0	2.1
0.3	1.0	77.5	6.7	11.4	2.0	21.1	0.3	1.1	0.3
1.8	0.3	97.7	0.0	0.0	0.0	0.0	–	0.0	2.3
1.8	1.0	39.3	17.0	30.9	7.3	55.2	0.4	3.7	1.8
0.3	HPβ-CD (0.25)	94.5	0.8	1.8	0.0	2.6	–	0.0	2.9
0.3	0.5	67.3	9.5	16.0	2.6	28.1	0.3	0.0	4.6

[a]Analyses by GC.
[b]Control represents without β-CD and its derivatives.

agents like sodium dithionite [18,19] and sodium borohydride [20].

Hence, an attempt was made in this present work to study the product distribution under various concentrations of alkali during hydrogenation of R-(+)-pulegone and $(2S,5R)$-(−)-menthone by Raney nickel in presence of β-cyclodextrin(β-CD), water insoluble β-cyclodextrin-epichlorohydrin polymer (β-CD-polymer), heptakis-2,6-di-O-methyl-β-cyclodextrin (DMβ-CD), hydroxypropyl-β-cyclodextrin and cetyltrimethylammonium bromide (CTAB).

1. Results and discussion

1.1. Pulegone

Pulegone was hydrogenated over Raney Ni in the presence of β-CD and its derivatives. The reduction was found to be facile in the presence of alkali. Hydrogen consumption profiles of pulegone were studied in the presence of alkali and β-CD and its derivatives (Table 1 and Fig. 1). Although the rate of hydrogen consumption in presence of alkali showed slightly less than two equivalents (to pulegone) of hydrogen, GC
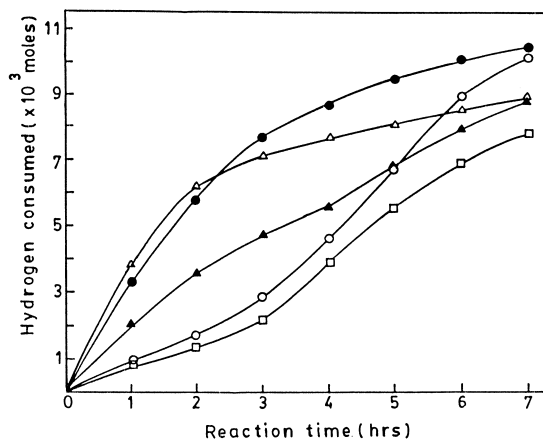

Fig. 1. Rates of hydrogen consumption by pulegone. Pulegone (6.2 moles) in alcohol with 0.5 ml of 40% NaOH and Raney Ni was used. Hydrogenation was carried out at room temperature and atmospheric pressure. ● — β-CD, ○ — control, △ — DMβ-CD, ▲ — β-CD-polymer, □ — CTAB.

analyses showed very little unreacted pulegone present in the reaction mixture. Hydrogenation was found to occur in two stages. Olefinic double bond (1–2 reduction) was found to reduce first fairly at a faster rate than the subsequent slower reduction of the keto group (1–4 reduction). The rate of reduction of the olefinic double bond was found to be faster for the β-CD and its derivatives mediated reactions, than the control and CTAB mediated reactions as deduced from the observed product profiles. Except for the control (absence of β-CD and its derivatives) and CTAB mediated reaction which showed a sigmoidal curve, the β-CD and its derivatives mediated reactions did not exhibit such a behaviour. While the reaction in the absence of alkali gave a higher ketone/alcohol ratio, that in the presence of alkali resulted in a lower ketone/alcohol ratio.

The reduction in presence of alkali was studied with various concentrations of alkali. To study the effect of alkali, the reduction was carried out with dilute (10% NaOH) and concentrated alkali (40% alkali).

Hydrogenation in absence of alkali and β-CD and its derivatives gave 3.4% of epimeric alcohols with a M/N (Menthol/Neomenthol) ratio of 3.3. The reaction in the presence of 1.0 equivalent β-CD resulted in 25.9% epimeric alcohols with the highest M/N value of 9.0. However, β-CD-polymer (6.5%), DMβ-CD (1.9%) and CTAB (3.4%) effected very low conversions. In the presence of 40% alkali, the control reaction (absence of β-CD and its derivatives) showed about 76.8% of menthol formation, which was higher in the presence of 1 equivalent of β-CD (89.8%). However, 1 equivalent of β-CD-polymer (57.5%), 0.5 equivalent of DMβ-CD (44.5%) and 1 equivalent of CTAB (38.0%) exhibited lesser conversions than the control.

The control reaction and that in presence of DMβ-CD showed 92.6% and 98.0% menthone/isomenthone respectively showing that the selectivity in reduction even in control was good. In case of β-CD polymer and CTAB,

menthol/neomenthol ratio was found to be low (2.1 for β-CD-polymer and 1.6 for CTAB).

An alkali concentration of 10% NaOH in various volumes was also employed. Hydrogenation in presence of 0.3 ml (10% NaOH) alkali produced maximum formation of menthols (42.2%) and menthones (44.1%) (Fig. 2). However, further increase in alkali concentration from 0.9 to 1.8 ml resulted in decrease in conversion of alcohols from 8.1% to 0.9%. Introduction of lesser concentration of alkali caused the formation of neoisomenthol, besides menthol and neomenthol. However, the menthol proportions were lower than those of neoisomenthol and neomenthol. Also, increase in concentration of alkali from 0.9 to 1.8 ml caused decrease in the amount of neomenthol, neoisomenthol and menthol.

Addition of 0.3 ml of 10% NaOH in the presence of 0.1 equivalent of β-CD to pulegone on hydrogenation enhanced the yield of alcohols to a maximum of 95.4% (neomenthol 40.8%, neoisomenthol 42.5% and menthol 12.1%). Maximum alcohol/ketone ratio (59.6) and maximum formation of menthol (12.1%) were observed at 0.1 equivalent β-CD with 0.3 ml alkali. Increase in alkali concentration from 0.6 to 1.5 ml at 0.1 equivalent of β-CD resulted in gradual decrease in percentage of alcohols from 87.7% to 20.4% with gradual decrease in neomenthol, neoisomenthol and menthol. Further, increase in alkali to 1.8 ml resulted in slight
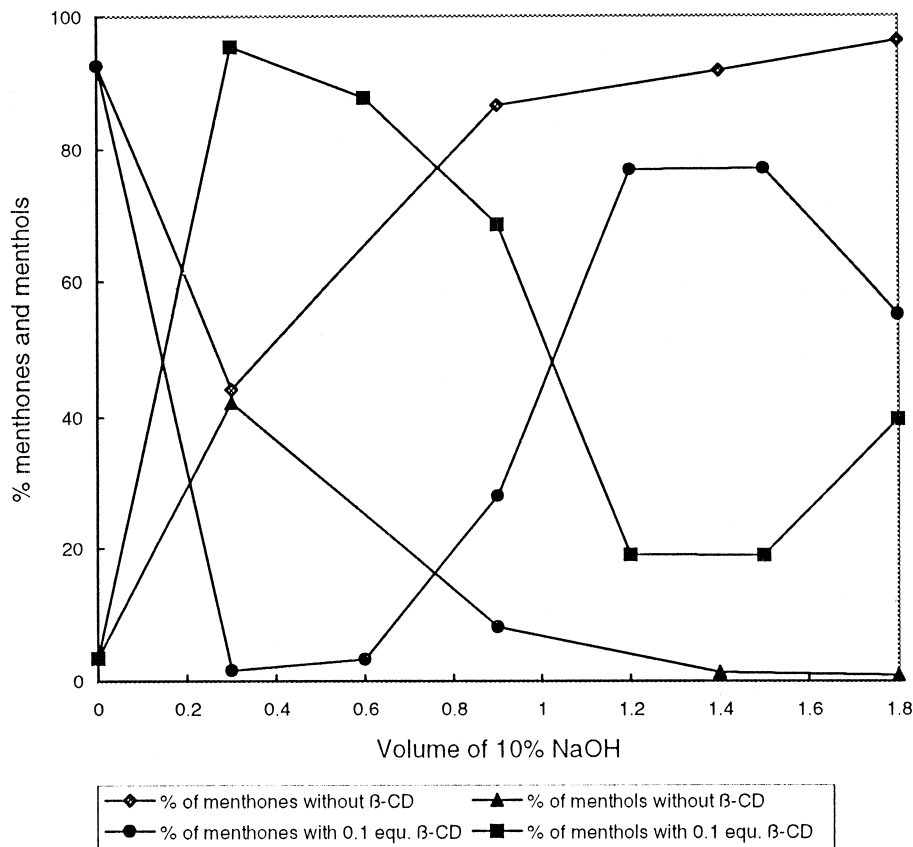

Fig. 2. Effect of alkali on hydrogenation of pulegone with and without β-CD. Pulegone (3.1 moles) in alcohol with various volumes of 10% NaOH and β-CD (0.1 equivalent) and Raney Ni was used. Hydrogenation was carried as in Fig. 1. ♦ —Percent of menthones without β-CD, ▲ —percent of menthols without β-CD, ● —percent of menthones with 0.1 equivalent β-CD, ■ —percent of menthols with 0.1 equivalent β-CD.

increase in alcohols to 39.6%. Thus, increase in alkali above 0.3 ml in the presence of 0.1 equivalent β-CD resulted in decrease in the yield of menthols and increase in the yield of menthones. However, increase in alkali with same β-CD concentration did not alter the M/N ratio.

Hydrogenation in the presence of 0.3 ml alkali with increase in β-CD concentration from 0.5 equivalent to 1.0 equivalent resulted in gradual decrease in the yield of alcohols from 37.8 to 21.1% (neomenthol 12.5 to 6.7%, neoisomenthol 21.8 to 11.4% and menthol 3.5 to 2.0%) and increase in ketones from 62.1 to 77.5% respectively (Fig. 3). Reaction with 1.8 ml alkali and 0.2 equivalent β-CD caused only olefinic double bond reduction giving rise to a maximum formation of menthones (97.7%). Further increase in the amount of β-CD to 1

equivalent with 1.8 ml alkali, resulted in increase in total percentage of alcohols from 0 to 55.2% with concomitant decrease in total percentage of ketones (from 97.7 to 39.3%).

Addition of 0.25 equivalent HPβ-CD with 0.3 ml alkali favoured reduction of olefinic double bond more. However, increase in HP β-CD to 0.5 equivalent with 0.3 ml alkali resulted in increase in the total yield of alcohols from 2.6 to 28.1%.

At equivalent concentration of alkali, presence of higher volume of alkali generally resulted in low percentage of alcohols and lower volume of alkali favoured the reduction of ketone, resulting in a higher percentage of alcohols. In general, increase in 10% alkali and increase in concentration of β-CD resulted in decrease in the formation of menthols. However, 1.8 ml of 10% alkali corresponding nearly
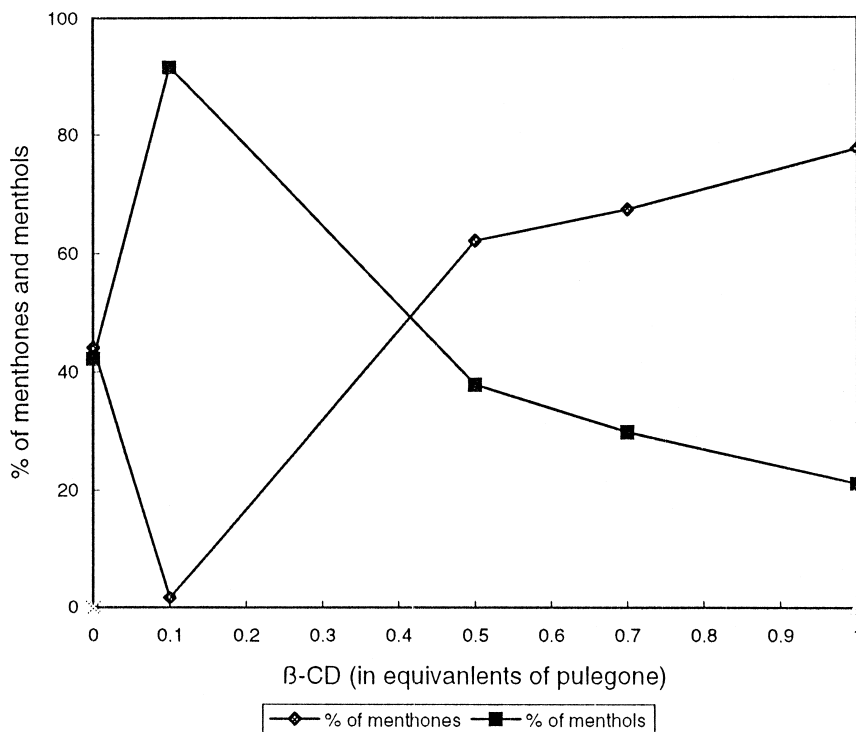

Fig. 3. Effect of β-CD on hydrogenation of pulegone in 0.3 ml alkali. Pulegone (3.1 moles), 0.3 ml 10% NaOH in alcohol with various equivalents of β-CD (to pulegone) and Raney Ni was used. Hydrogenation was carried as in Fig. 1. ◆ —Percent of menthones, ■ —percent of menthols.

to 0.5 ml of 40% NaOH gave better yield of menthols (55.5%) even with 0.1 and 1.0 equivalent of β-CD.

1.2. Menthone

The results obtained from the reduction of menthone are shown in Table 2. The rates of hydrogen consumption under alkaline conditions (40% alkali) by menthone in presence of β-CD, β-CD-polymer, DM-β-CD and CTAB are shown in Fig. 4. Except for the reaction in the presence of DM-β-CD and β-CD-polymer, the rates of reduction in the presence of β-CD,

CTAB and control reactions showed sigmoidal behavior. With the exception of the control reaction, the rates of hydrogen consumption in the initial stages were higher for reactions in the presence of β-CD, β-CD-polymer, CTAB and DMβ-CD.

It was very difficult to reduce ketones in the absence of alkali using Raney Ni without any additive. It can be seen from Table 2 that hydrogenation in the absence of alkali resulted in very low yield of alcohols (13.2%) in the control reaction. The reaction in presence of 1.0 equivalent β-CD and β-CD-polymer resulted in 56.7% and 17.7% epimeric alcohols respec-

Table 2
Effect of alkali and β-CD and its derivatives on the hydrogenation of menthone over Raney Ni[a]

NaOH in ml	Catalyst in molar equivalents of ketone	Unreacted menthone	Neo-menthol	Neoiso-menthol	Menthol	Total	Menthol/ Neomenthol ratio
Without alkali							
	Control[b]	85.4	5.1	1.8	6.3	13.2	1.24
	β-CD (0.1)	59.9	7.9	4.3	26.0	38.3	3.3
–	β-CD (1.0)	43.3	32.7	0.0	24.0	56.7	0.7
–	β-CD-polymer (1.0)	82.3	11.7	0.0	6.0	17.7	0.5
–	DMβ-CD (1.0)	100.0	0.0	0.0	0.0	0.0	–
–	CTAB (0.5)	8.6	28.6	0.0	62.8	91.3	2.2
With 40% alkali							
0.1	Control[b]	44.7	26.6	0.0	28.7	55.3	1.1
0.1	β-CD (1.0)	0.3	17.1	0.0	82.6	99.7	4.8
0.1	β-CD-polymer (1.0)	8.2	27.5	0.0	64.3	91.8	2.3
0.1	DM-β-CD (1.0)	64.5	10.5	0.0	25.0	35.5	2.4
0.1	CTAB (0.5)	2.7	27.7	0.0	69.6	97.3	2.5
With 10% alkali							
0.1	–	7.9	57.8	12.5	21.0	78.9	0.3
0.2	–	0.3	58.7	17.9	21.5	98.1	0.4
0.3	–	8.0	40.9	36.0	14.1	91.0	0.3
0.4	–	14.7	33.8	38.5	12.2	84.5	0.3
0.6	–	20.5	30.5	35.4	12.2	78.1	0.4
0.8	–	53.1	18.1	20.6	7.9	46.6	0.4
0.1	β-CD 0.1	8.0	58.4	11.2	22.0	91.4	0.4
0.2	0.1	1.8	56.2	21.3	20.1	97.6	0.4
0.3	0.1	5.4	46.1	30.5	17.3	93.9	0.4
0.4	0.1	7.2	33.0	39.3	19.3	91.6	0.6
0.6	0.1	8.3	33.1	40.9	13.7	87.7	0.4
0.2	0.2	31.7	40.9	11.5	15.7	68.1	0.4
0.2	0.4	18.9	47.3	9.8	24.0	81.1	0.5
0.2	0.5	14.2	42.2	9.4	34.2	85.8	0.8
0.2	1.0	13.6	41.2	9.2	35.2	85.6	0.9

[a] By GC analyses.
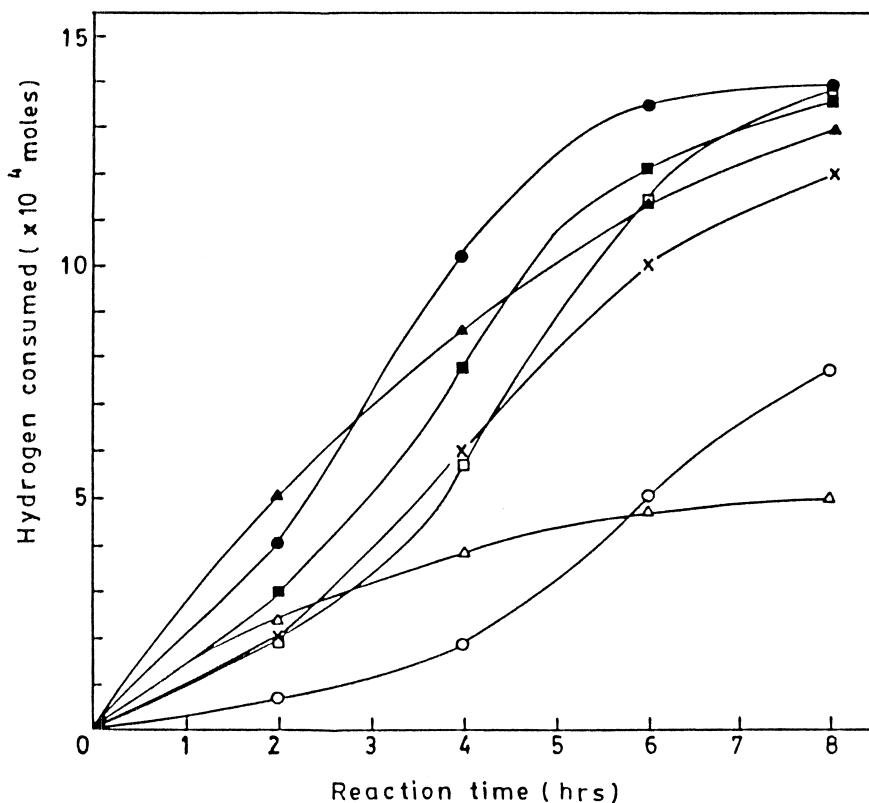[b] Control represents without β-CD and its derivatives.

Fig. 4. Rates of hydrogen consumption by menthone. Menthone (1.16 moles) in alcohol with 0.1 ml of 10% NaOH and Raney Ni was used. Hydrogenation was carried as in Fig. 1. ● —β-CD, ○—control, △ —DMβ-CD, ▲ —β-CD-polymer, □—CTAB, ■ —β-CD (0.5 equivalent), × —β-CD (0.1 equivalent).

tively. However, presence of 0.1 equivalent of β-CD resulted in 38.3% menthols. Presence of DMβ-CD did not show any conversion of ketone. But in case of 0.5 equivalent CTAB, the amount of epimeric alcohols formed was 91.3%. With increase in β-CD, the proportions of epimeric menthols formed increased from 38.3% for 0.1 equivalent of β-CD to 56.7% for 1.0 equivalent of β-CD.

When the reduction was carried out in presence of 40% alkali, the formation of menthols were found to be higher. While the reaction in presence of alkali and in absence of β-CD and its derivatives showed 55.3% of menthols formation, the reduction in presence of β-CD and β-CD polymer gave 99.7% and 91.8% menthols, respectively. However, the reduction in presence of DMβ-CD showed only 35.5% men-

thols. The reduction in presence of 0.5 equivalent of CTAB also showed better conversion (97.3%).

Since alkali was shown to increase the formation of menthols, this aspect was further investigated in detail. Instead of 40% NaOH employed, the reactions were carried out with 10% NaOH such that the alkali concentration remained the same. Fig. 5 shows the effect of 10% NaOH on the extent of conversion with and without 0.1 equivalent of β-CD. At all levels of NaOH, the proportions of menthols formed were found to be higher in the presence of 0.1 equivalent of β-CD. However, in both presence and absence of β-CD, maximum menthol formation was detected at 0.2 ml of 10% NaOH (97.6 and 98.1%, respectively), thereafter, the proportions of menthols decreased with
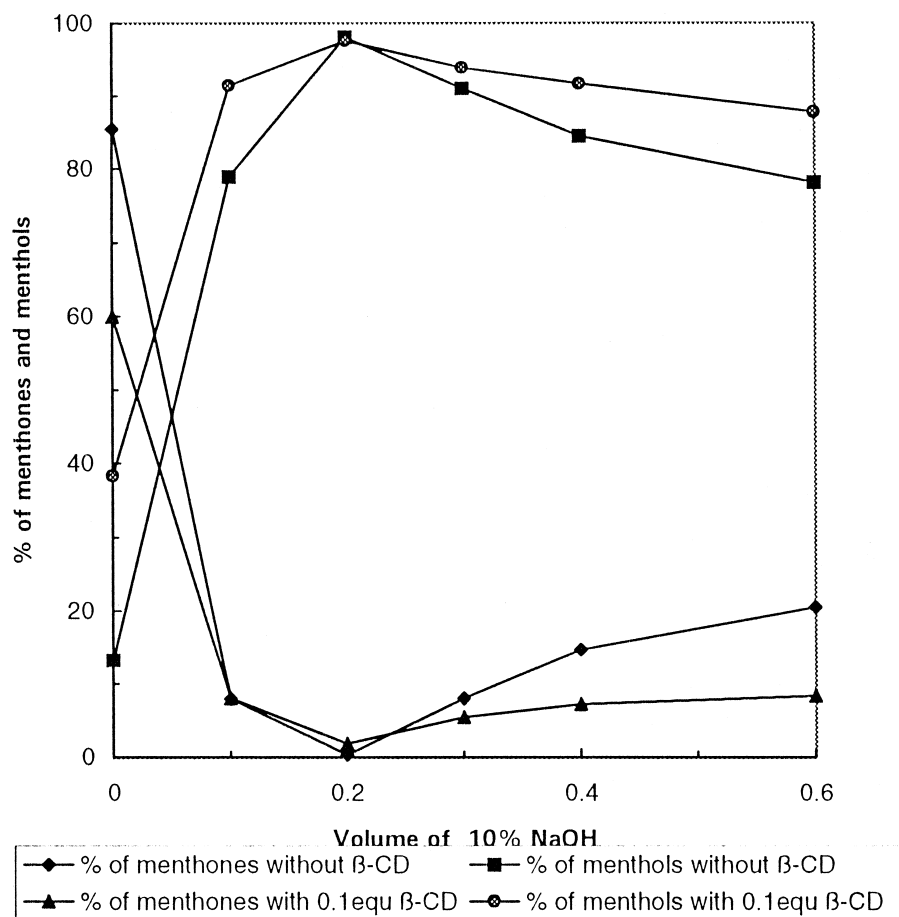
Fig. 5. Effect of alkali on hydrogenation of menthone with and without β-CD. Menthone (1.16 moles), β-CD (0.1 equivalent to menthone) in alcohol with various volumes of 10% NaOH and Raney Ni was used. Hydrogenation was carried as in Fig. 1. ♦—Percent of menthones without β-CD, ■—percent of menthols without β-CD, ▲—percent of menthones with 0.1 equivalent β-CD, ●—percent of menthols with 0.1 equivalent β-CD.

increase in NaOH. However, at 0.2 equivalent of β-CD, the amount of menthols formed was the lowest at 68.1%. Above and below these levels, higher proportions of menthols were observed. In the presence of 0.2 ml NaOH, increase in β-CD from 0.2 to 1 equivalent resulted in increase of menthols formation from 68.1% to 85.6% (Fig. 6).

Neoisomenthol formation was also detected in all these cases. Increase in alkali from 0.1 ml to 0.6 ml resulted in increase in the formation of neoisomenthol both in the absence and presence of β-CD. However, increase in β-CD at 0.2 ml alkali decreased the formation of neoisomenthol.

Although, Fig. 5, showed marginal increase in alcohol formation at all levels of NaOH, in the presence of β-CD, the proportion of menthol was always higher than the proportion of the neoisomenthol (Fig. 7). However, the highest M/N ratios were observed with control (1.24) (absence of β-CD as well as absence of alkali) and for the reaction in presence of 0.1 equivalent of β-CD but in the absence of alkali (3.3). In all the other cases, the M/N ratios were lower than 1 due to higher proportion of neomenthol than menthol.

Since absolute alcohol was employed for the catalysis in both pulegone and menthone, presence of excess water in NaOH was found to
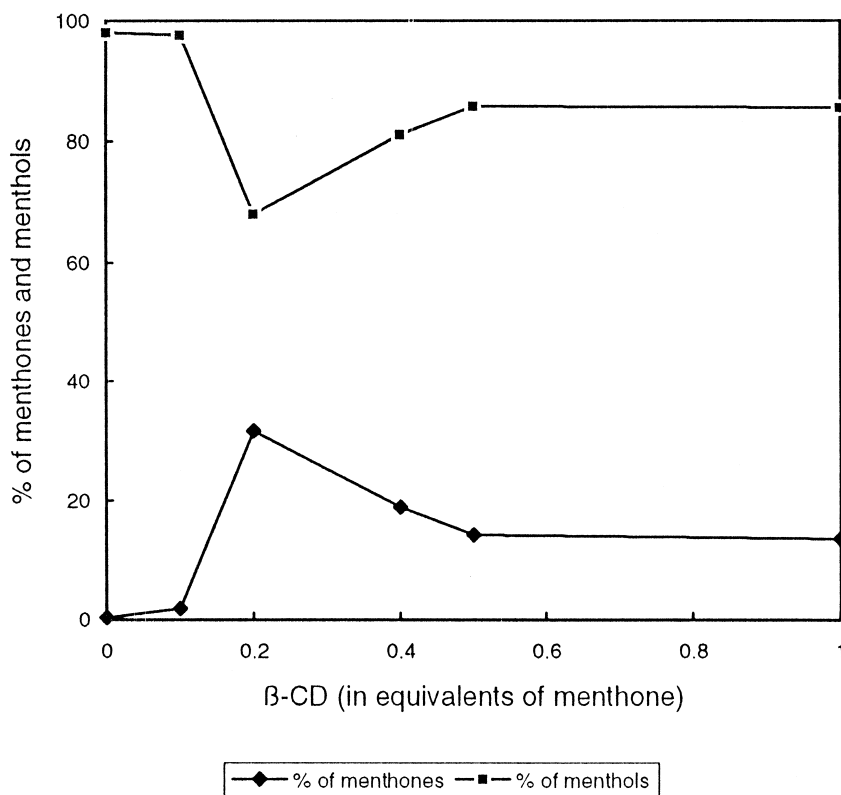
Fig. 6. Effect of β-CD on hydrogenation of menthone with 0.2 ml alkali. Menthone (1.16 moles), 0.2 ml of 10% NaOH in alcohol with β-CD (in various equivalents to menthone) and Raney Ni was used. Hydrogenation was carried as in Fig. 1. ♦ —Percent of menthones, ■ —percent of menthols.

affect the extent of conversion and menthol formation.

A significant feature of β-CD was that it progressively increased the amount of menthol formation and drastically reduced the formation of neomenthol and neoisomenthol when the reduction was carried out in the presence of 40% alkali both incase of pulegone and menthone (Tables 1 and 2). Therefore, it is clear that β-CD has a positive control over the epimerisation and conversion of menthol. The mechanism of the hydrogenation of menthone is not known. Cumulative effect of the orientation of menthone or pulegone inside the cyclodextrin cavity on one hand and that of the complex on the Raney Ni surface on the other hand probably may be the reason for the alteration in the proportion of compounds.

The inclusion complex formation studies by ultraviolet–visible spectroscopy exhibited a binding constant value of 5428 ± 500 M^{-2} for the 1:2 β-CD:pulegone complex and 937 ± 50 M^{-2} for the 1:2 complex formed between DM β-CD and pulegone [19].

Addition of metals (Ni, Cu, Mn, Cr), triethylamine, amino acids, base, catalyst support, additives or impurities, in many cases, act as promoters and increases the efficiency of the Raney Ni catalyst [21]. In a similar way, addition of β-CD and its derivatives also seem to act as promotors and the mechanism is uncertain. A probable mode of action may be that, β-CD and its derivatives may be brought close to the Raney Ni surface, which may indirectly bring the included guest molecule nearer to the metal surface for the action of adsorbed hydro-
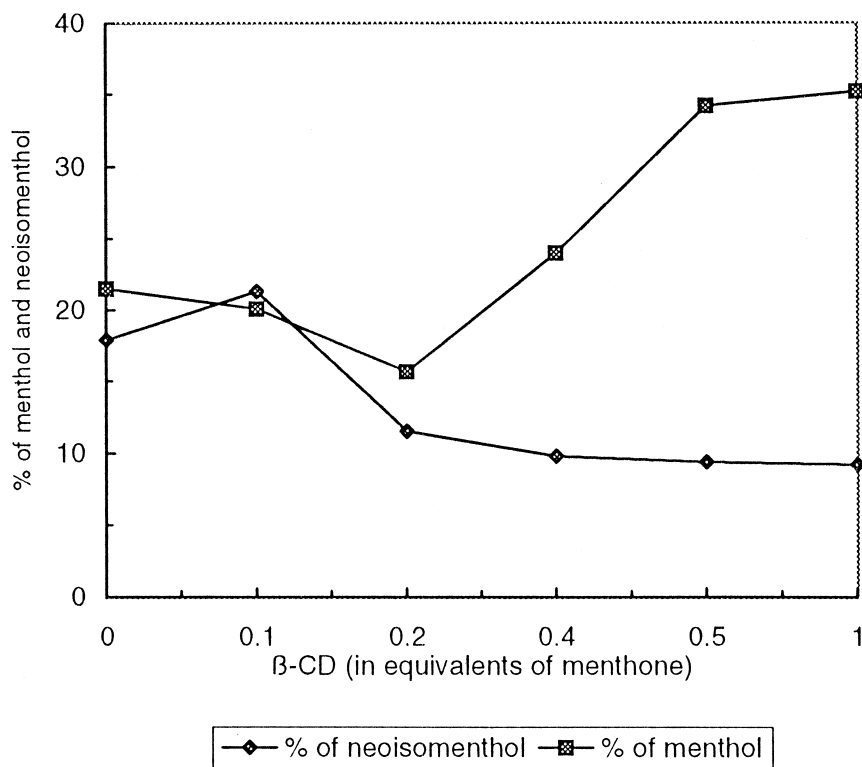
Fig. 7. Effect of β-CD on the formation of menthol and neoisomenthol on hydrogenation of menthone with 0.2 ml alkali. Menthone (1.16 moles), 0.2 ml of 10% NaOH with β-CD (in various equivalents to menthone) and Raney Ni was used. Hydrogenation was carried as in Fig. 1. ♦ —Percent of neoisomenthol, ■ —percent of menthol.

gen. Alkali also has a better role to play besides aiding the reduction of the keto groups. Since β-CD exhibits a pk_a value of $\approx$ 12.1 [22] alkoxy anion arising due to dissociation of secondary hydroxyl groups on C-2 and C-3 of β-CD may aid better in forming a stronger complex by increase in hydrogen bonding propensities than the unionised molecule, thereby leading to better conversion rates.

Formation of a 1:2 (β-CD: pulegone) complex with β-CD and DM-β-CD, is the reason why 0.5 equivalent of DM-β-CD gave rise to chemoselectivity ($\approx$ 98%) in the pulegone reduction to exclusively menthone. Presence of two pulegone molecules inside β-CD cavity may lead to different orientations for pulegone, head to head, head to tail or tail to tail. It is not clear which orientation is more preferred, from the present investigation. However, some of

these orientations probably result in restriction of hydrogen transfer from the surface of nickel to react with the double bond and keto groups of pulegone and menthone. Dissociation of secondary hydroxyl groups of β-CD in presence of alkali may also change the orientation of the guest ketone and the stoichiometries of the complexes, affecting the distribution of reduction products formed.

2. Experimental

(R)-(+)-pulegone purchased from Aldrich Chemical, USA was used without further purification. β-CD was a gift from American Maize Products, USA. β-CD-polymer and DM-β-CD were prepared according to the procedures of Shaw et al. and Szejtli et al., respectively. Raney

Ni was prepared according to the method described by Vogel. $(-)$-menthone was prepared by the oxidation of $(-)$-menthol by chromic acid.

A typical procedure employed for the hydrogenation reaction is as follows. Pulegone (6.2 moles) or menthone (1.16 moles) was taken in 20 ml absolute ethanol in a glass hydrogenation flask, along with about 1 ml of Raney Ni suspension (≈ 0.6 g) and with or without 0.5 ml (0.1 ml in case of menthone) of 40% NaOH or various volumes of 10% NaOH. The flask was filled with hydrogen gas at a pressure of 1.37 atmospheres, after evacuation of air and set mechanically agitated for 8 h. The Raney Ni catalyst was then filtered off, and the filtrate acidified and extracted with ether, dried and concentrated.

The product distribution of the reaction mixture was analysed by GLC, using a Hewlett-Packard 5730 A instrument, fitted with a carbowax 20 M, 6 ft column, maintained at $110°C$, with a 30 ml/min nitrogen flow rate. The injection and detection port temperatures were maintained at $200°C$ and $250°C$ respectively. Retention times (RT): pulegone = 19.0 min, menthone = 8.2 min, isomenthone = 9.3 min, menthol = 16.7 min, neomenthol = 13.4 min, neoisomenthol = 15.4 min. The reaction products were separated by column chromatography on silica gel, using hexane as the eluent and were characterised by comparing there m.p., $[\alpha]_D^{20}$, IR, ^{1}H-NMR and GLC with the authentic samples. The products obtained were optically pure $(-)$-menthone, $(-)$-menthol and $(+)$-neomenthol.

The rate of consumption of hydrogen by both pulegone and menthone were determined by monitoring the decrease in hydrogen pressure in the glass hydrogenation flask with time. The relation, $P_2 V_2 T_1 / T_2 P_1$ 22 400, gave the initial and final hydrogen concentration in the flask, in moles, the difference of which showed the amount of hydrogen consumed by the compound. P_2 is the initial pressure and pressure after time t hours, $V_2 = 225$ ml, the volume of the glass flask, T_1 and P_1 are standard temperature and pressure.

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