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Optical Rotatory Dispersion Studies

LXX *. Anomalous Rotatory Dispersion of Xanthates: Application in Stereochemical Studies of Alcohols

BERNDT SJÖBERG**

Department of Organic Chemistry, Chemical Institute, University of Uppsala, Uppsala, Sweden

DONALD J. CRAM

Department of Chemistry, University of California, Los Angeles, Calif.

LYNN WOLF and CARL DJERASSI

Department of Chemistry, Stanford University, Stanford, Calif., U.S.A.

Submitted in honour of the sixtieth birthday of Professor *Arne Fredga*

The optical rotatory dispersion of several xanthates has been investigated. The spectroscopic properties of xanthates with absorption bands of low extinction around 355 mμ make them very desirable chromophoric derivatives for anomalous rotatory dispersion measurements among the "transparent" alcohols. The xanthates can be used for stereochemical correlations. The relative configurations of alcohols and their corresponding amines can also be established through the anomalous rotatory dispersion curves of their xanthate and dithiocarbamate derivatives.

Optical rotatory dispersion curves have recently found important applications in many areas of chemistry [1,2]. Plain curves [3] are sometimes quite useful for configurational assignments [4,5] and are to be preferred over monochromatic rotation measurements. However, the most important applications of optical rotatory dispersion measurements in organic chemistry have been

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* Paper LXIX, Beard, C., Djerassi, C., Elliott, T. and Tao, R.C.C. *J. Am. Chem. Soc.* **84** (1962) 874.

** Present address: AB Astra, Södertälje, Sweden.

on compounds possessing Cotton effects[1]. Such anomalous dispersion curves are only shown by substances with optically active chromophores absorbing in a presently accessible spectral range, preferably with relatively low extinction (*e.g.*, C=O, C=S, N=O chromophores). There are, however, a number of important classes of organic compounds (*e.g.*, alcohols, amines, carboxylic acids) that do not satisfy these requirements. In order to circumvent this difficulty, we have been searching for easily prepared "chromophoric" derivatives of the "nonchromophoric" parent compound. Thus dithiocarbamates[6] and N-thionocarbethoxy derivatives[7] of α-amino acids as well as xanthates of α-hydroxy acids[6] have been excellent for this approach. The spectroscopic properties of the C=S chromophore have proved to be useful also in a number of other environments[1b], for example in thiourea derivatives of carboxylic acids[8].

Whilst simple alcohols are substantially transparent within the range of quartz spectrographs (the absorption band lies near 185 mμ), xanthates (λ max *ca.* 350 mμ, ε *ca.* 60) satisfy the relevant spectroscopic requirements for anomalous rotatory dispersion studies*. Tschugaeff investigated several dixanthates[9] and subsequently[10] xanthates and dithiourethanes of menthol, borneol, and fenchol. Instrumental limitations precluded rotatory dispersion measurements of xanthates through the region of absorption, and only some 20 years later Lowry and Hudson[11] could demonstrate Cotton effects of a few xanthates. However, no attempts were made to use these anomalous dispersion curves for stereochemical correlations. It was with this latter purpose in mind that we undertook a more extensive rotatory dispersion study of xanthates of a variety of alcohols. Preliminary observations were reported earlier[1a], and details will now be given in the present paper.

The rather high amplitudes observed[11] for xanthates of the cyclic alcohols borneol and fenchol were somewhat fortuitous, since the amplitudes and at times even the appearance of Cotton effects of xanthates are very dependent upon chemical constitution. The methyl xanthate (I) and N-phenyl-N-thiobenzoylthiourethane (II) of 2-methylbutanol exhibit only plain dispersion curves (Fig. 1), and if there are any Cotton effects corresponding to the absorption bands at 350 and 510 mμ, respectively, the amplitudes must be extremely small and within experimental error. The situation is quite altered when the alcohol has a more rigid or bulky structure giving a greater interaction between the C=S chromophore and the various substituents of the molecule. The dispersion curve (Fig. 2) of methyl (−)-1-phenyl-2,2-diphenylethyl xanthate (III) thus has a very pronounced negative Cotton effect with a trough of $[\alpha]_{380}$ −1290° and a peak of $[\alpha]_{335}$ +520°, and similarly N-dithiocarbomethoxy (−)-1-phenyl-2,2-diphenylethylamine (IV) has a negative Cotton effect centered around the dithiocarbamate absorption band at 330 mμ**. The establishment of stereochemical relationships between alcohols and amines or hydroxy and amino acid by chemical interrelations is sometimes complicated[12]. However, it has

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* For a discussion of electronic absorption spectra of various thiono compounds, see Janssen, M.J. *Rec. Trav. Chim* **79** (1960) 454.

** Conclusive proof for the configurations III and IV of the two compounds has been obtained by several independent methods; see Ref. [29].

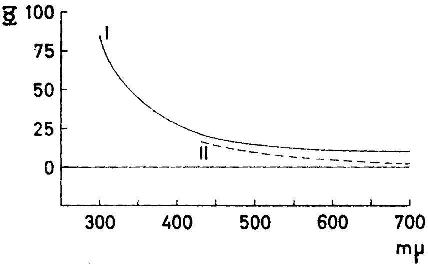

Fig. 1. Optical rotatory dispersion curves of methyl L-2-methylbutyl xanthate (I) and L-2-methylbutyl N-phenyl-N-thiobenzoyl-thiourethane (II).

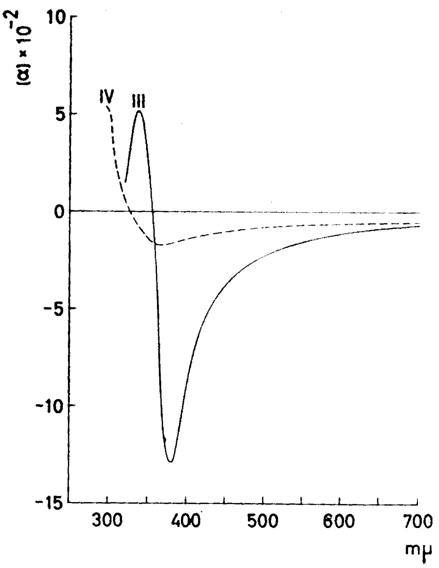

Fig. 2. Optical rotatory dispersion curves of methyl L-1-phenyl-2,2-diphenylethyl xanthate (III) and N-dithiocarbomethoxy L-1-phenyl-2,2-diphenylethylamine (IV).

been shown,[6] that the rotatory dispersion method affords extremely convenient means of assigning configurations to pairs of α-hydroxy and α-amino acids, as the sign of the Cotton effect of the α-hydroxy acid xanthate corresponds to the sign of the Cotton effect of the configurationally related α-amino acid dithiocarbamate. Generally pairs of alcohols and amines can be configurationally related in a similar way by means of the rotatory dispersion curves of their dithiocarbalkoxy derivatives. Dithiocarbalkoxy derivatives of very simple compounds (*e.g.*, 2-methyl-butanol) will apparently not give any Cotton effects, but it would appear that the signs of the plain dispersion curves can be used for stereochemical purposes in an analogous manner to the plain curves of simpler carboxylic acids [4].

Cram and collaborators, in connection with their extensive stereochemical studies,[13] have prepared several diastereoisomeric alcohols of known relative configurations, and in most cases they have also established the absolute configurations. Xanthates of several of these alcohols have now been prepared and their rotatory dispersion investigated in order to see if configurations and conformations could be correlated to any special features of the dispersion curves. Cotton effects with quite large amplitudes are found (Figs. 3—5) for the methyl xanthates V—XIII. The compounds in Fig. 3, all of the L-configuration*, have very similar negative Cotton effect curves with troughs

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* The conventions, previously adopted are used, see Cram, D. J. *J. Am. Chem. Soc.* **74** (1952) 2149; Elhafez, F.A.A. and Cram. D. J. *J. Am. Chem. Soc.* **74** (1952) 5846.

around 367 mμ and peaks at 330 mμ. Changes at the α-carbon (*e.g.*, methyl to ethyl to phenyl, V to VI to VII) will apparently not affect the sign of the dispersion curves. Variations at the β-carbon such as methyl to ethyl (V to VIII) or phenyl to cyclohexyl (V to IX) similarly will not change the sign of the dispersion curves as the two L-*threo* compounds (VIII and IX) have negative Cotton effects (Fig. 4). In view of these observations it seems probable that simultaneous variations in substituents both at the α- and β-carbons will be possible without changing the sign of the Cotton effects. The absolute configuration of XIII has been established [14] and the negative Cotton effect indicates that the compound belongs to the L-series. When the configuration is arranged at the α-carbon to give the L-*erythro* compounds (X and XI), positive Cotton effect curves are found (Fig. 5). The absolute configuration of the *erythro* compound (XII) has not previously been established, but considering the similarity in the dispersion curves of XI and XII (Fig. 5) in conjunction with the observations on the xanthates V, VI and VII, we suggest the L-configuration for XII.

Most of the naturally occurring alcohols are cyclic, and we considered it important therefore, to investigate rotatory dispersion curves of xanthates in several different cyclic environments. Rotatory dispersion curves of the methyl xanthates of *cis*- and *trans*-2-methylcyclohexanol (XIV and XV) are shown in Fig. 6, both having negative Cotton effects. The *cis* alcohol was prepared and resolved through the strychnine salt of the acid phthalate according to Gough, Hunter, and Kenyon [15], but for our studies it was not necessary to obtain the pure antipode and an alcohol with the rotation $[\alpha]_D + 4.85°$ (neat) was used. Kenyon *et al.* reports $[\alpha]_D + 12.4°$ (neat) for the optically pure alcohol.

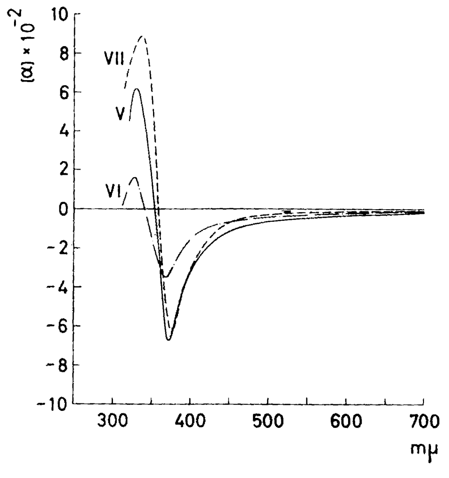

Fig. 3. Optical rotatory dispersion curves of methyl L-*threo*-3-phenyl-2-butyl xanthate (V), methyl L-*threo*-4-phenyl-3-pentyl xanthate (VI) and methyl L-*erythro*-1,2-diphenylpropyl xanthate (VII).

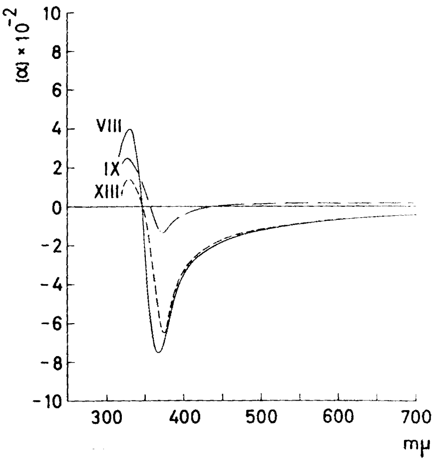

Fig. 4. Optical rotatory dispersion curve of methyl L-*threo*-3-phenyl-2-pentyl xanthate (VIII), methyl L-*threo*-3-cyclohexyl-2-butyl xanthate (IX) and methyl *erythro*-1,2-diphenyl-2-methylbutyl xanthate (XIII).

The racemic *trans*-2-methylcyclohexanol was obtained from commercial 2-methylcyclohexanol by repeated recrystallization of its half phthalate. Since convenient resolutions of alcohols have recently been reported [16,17] through the 3β-acetoxy-Δ^5-etienates we prepared and recrystallized *trans*-2-methylcyclohexanol 3β-acetoxy-Δ^5-etienate. For preparation of the xanthate an alcohol was used with the rotation $[\alpha]_D$ $+5.27°$ (neat), Kenyon reports $[\alpha]_D$ $+34.38°$ (neat) for the optically pure form. At the time that our work was undertaken the absolute configuration of the two epimeric alcohols were not known, but their relative stereochemistry was easily established by oxidation to the corresponding ketone. The *cis*-alcohol gave a ketone having a negative Cotton effect and the *trans*-alcohol a positive*, thus showing that XIV and XV are antipodal around the methyl group, a conclusion in agreement with Kenyon's results [15]. It follows that xanthates of the 2-methylcyclohexanol series exhibit Cotton effects of identical sign, if their hydroxyl-bearing centers possess identical absolute configurations.

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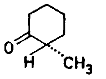
* As a result of recent work (Paper LXIX in this series), we now know, that (+)-2-methylcyclohexanone with a positive Cotton effect possesses the following absolute configuration:



Consequently, XIV and XV represent correct absolute stereoformulas.

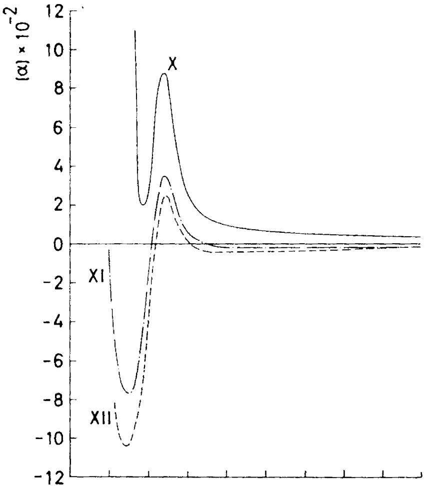


Fig. 5. Optical rotatory dispersion curves of methyl L-*erythro*-3-phenyl-2-butyl xanthate (X), methyl L-*erythro*-3-phenyl-2-pentyl xanthate (XI) and methyl *erythro*-1,2-di(isopropyl)-2-phenylethyl xanthate (XII).

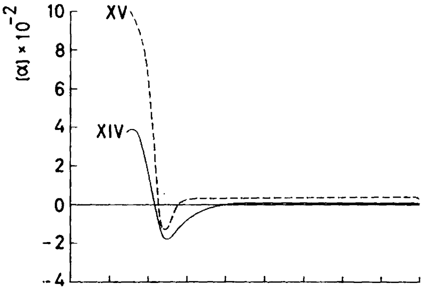
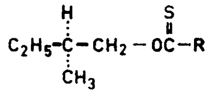


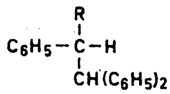
Fig. 6. Optical rotatory dispersion curves of methyl *cis*-2-methylcyclohexyl xanthate (XIV) and methyl *trans*-2-methylcyclohexyl xanthate (XV).



$C_2H_5-\overset{H}{\underset{CH_3}{C}}-CH_2-O\overset{S}{\overset{\|}{C}}-R$

I $R = CH_3S$

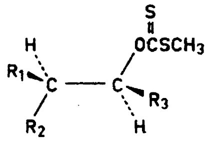
II $R = C_6H_5\underset{S}{\underset{\|}{C}}-\underset{C_6H_5}{N}$

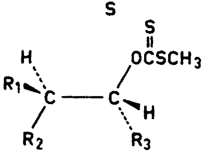


$C_6H_5-\overset{R}{\underset{CH(C_6H_5)_2}{C}}-H$

III $R = CH_3S\underset{S}{\underset{\|}{C}}O$

IV $R = CH_3S\underset{S}{\underset{\|}{C}}NH$





V $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = CH_3$

VI $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = C_2H_5$

VII $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = C_6H_5$

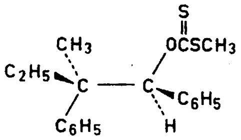
VIII $R_1 = C_2H_5$; $R_2 = C_6H_5$; $R_3 = CH_3$

IX $R_1 = CH_3$; $R_2 = C_6H_{11}$; $R_3 = CH_3$

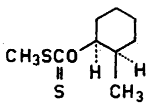
X $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = CH_3$

XI $R_1 = C_2H_5$; $R_2 = C_6H_5$; $R_3 = CH_3$

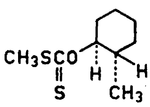
XII $R_1 = (CH_3)_2CH$; $R_2 = C_6H_5$; $R_3 = CH(CH_3)_2$



XIII



XIV



XV

Optically active *cis*- and *trans*-3-methylcyclohexanols of known configurations have been prepared by Hückel and Kurz [18] from (+)-3-methylcyclohexanone, which is easily obtainable [19] from pulegone. From either of these two alcohols we have prepared the methyl (XVI and XIX) and trityl (XVII and XX) xanthates as well as the N-phenyl-N-thiobenzoylthiourethanes (XVIII and XXI). The three derivatives in the *cis*- series are shown in Fig. 7 and those derived from the *trans*-alcohol in Fig. 8. As can be seen the methyl xanthates have both negative Cotton effects with very low amplitudes, while the trityl xanthates have positive Cotton effects of somewhat larger amplitudes. The N-phenyl-N-thiobenzoylthiourethanes both give rotatory dispersion curves with strong positive Cotton effects centered around the low intensity absorption band at 512 mμ. It is interesting to note that the rotatory dispersion curves of the trityl derivatives show opposite signs of the Cotton effects to those of their corresponding methyl xanthates. The reason for this behavior as well as why the *cis*- and *trans*-xanthate derivatives in the 2-series give opposite signs of the Cotton effects while in the 3-series the corresponding *cis* and *trans*-derivatives give the same will be discussed in the last section of this paper.

The menthols are cyclohexanols with an alkyl substituent in the 2-position on one side and another alkyl group in the 3′-position on the opposite side of the hydroxyl function. Thus in the menthol series it will be possible to examine the

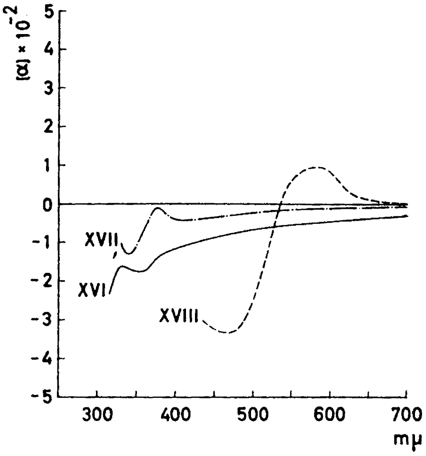


Fig. 7. Optical rotatory dispersion curves of methyl *cis*-3-methylcyclohexyl xanthate (XVI), trityl *cis*-3-methylcyclohexyl xanthate (XVII) and *cis*-3-methylcyclohexyl N-phenyl-N-thiobenzoylthiourethane (XVIII).

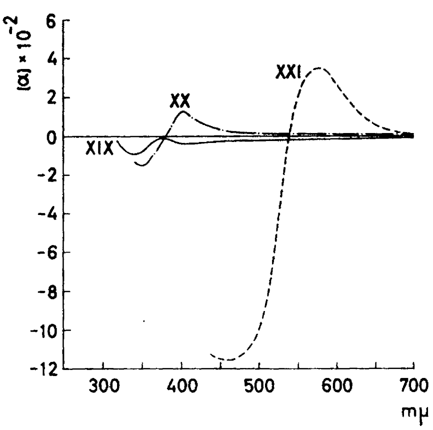


Fig. 8. Optical rotatory dispersion curves of methyl *trans*-3-methylcyclohexyl xanthate (XIX), trityl *trans*-3-methylcyclohexyl xanthate (XX) and *trans*-3-methylcyclohexyl N-phenyl-N-thiobenzoylthiourethane (XXI).

interaction of the two alkyl substituents. For this reason we prepared xanthates of menthol, isomenthol and carvomenthol. The methyl xanthate of (—)-menthol (XXII) exhibits a positive Cotton effect[11], and so does the methyl xanthate of (—)-carvomenthol (XXV) while the same derivative (XXIV) of (+)-isomenthol has a negative one (Fig. 9). The absolute configurations of menthol and isomenthol[20] as well as of carvomenthol[21] have been established beyond doubt. Both in menthol and isomenthol the isopropyl groups are *trans* to the hydroxyls while the hydroxyls and methyls bear a *cis* relationship in menthol and a *trans* relationship in isomenthol. When the methylgroup in the 3'-position (counted from the hydroxyl) is changed from *cis* in (—)-menthol to *trans* in (+)-isomenthol the signs of the Cotton effects are changed from positive for (—)-menthyl methyl xanthate (XXII) to negative for (+)-isomenthyl methyl xanthate (XXIV), an observation which seems consistent with the explanation given at the end of the discussion sections.

Jones and Klyne[5] have studied the plain rotatory dispersion curves of some steroid alcohols as well as of their acetates and benzoates. The intrinsic disadvantage of plain dispersion[1] curves over anomalous ones for complicated molecules prompted us to investigate if the xanthates of steroid alcohols would give suitable Cotton effect curves. As is shown in Fig. 10 the methyl xanthate (XXVI) and trityl xanthate (XXVII) of cholestan-3β-ol exhibit Cotton effect curves of very small amplitude. Considerably larger amplitudes were found[22] for the methyl xanthates of 5α-pregnan-20-ols, these derivatives offering an excellent means of differentiating between 20α- and 20β-ols as the 20α-xanthate exhibits a strong negative Cotton effect and the 20β-xanthate an equally

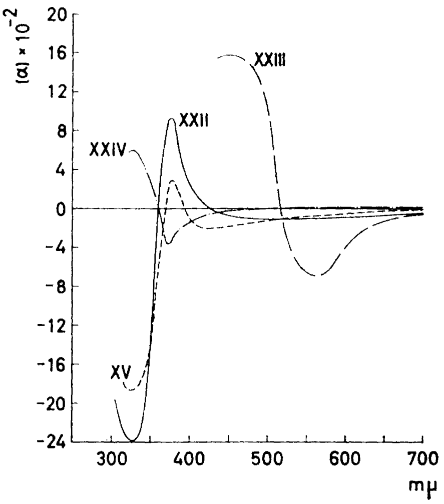


Fig. 9. Optical rotatory dispersion curves of methyl menthyl xanthate (XXII), menthyl N-phenyl-N-thiobenzoylthiourethane (XXIII), methyl isomenthyl xanthate (XXIV) and methyl carvomenthyl xanthate (XXV).

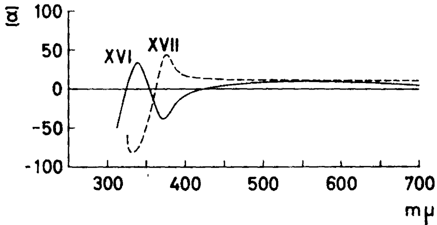


Fig. 10. Optical rotatory dispersion curves of methyl β-cholestanyl xanthate (XXVI) and trityl β-cholestanyl xanthate (XXVII).

strong positive one. As in the cyclohexanol series the methyl and trityl xanthate of cholestan-3β-ol have opposite Cotton effects, and this will be discussed further below.

Already Tschugaeff and Ogorodnikoff studied the rotatory dispersion curves of bornyl methyl xanthate (XXIX)[10a] and bornyl N-phenyl-N-thiobenzoylthiourethane (XXXI)[10b]. They found a positive Cotton effect in the visible wave-length range for the thiourethane, but they were not able to measure below 460 mμ and only obtained the plain part of the dispersion curve for the methyl xanthate. We have now prepared methyl and trityl xanthates and also N-phenyl-N-thiobenzoylthiourethanes of borneol and isoborneol. The optical rotatory dispersion curves of the three derivatives of borneol are found in Fig. 11 (XXIX and XXXI having been measured earlier by Lowry and Hudson[11]) and those of isoborneol in Fig. 12. The methyl xanthate of borneol (XXIX) exhibits a negative Cotton effect with a trough at 380 mμ and a peak at 330 mμ. The Cotton effect is thus almost exactly centered around the low intensity absorption band at 356 mμ. The rotatory dispersion curve of isobornyl methyl xanthate (XXXIII) shows a positive Cotton effect with a peak at 375 mμ and a trough at 330 mμ, this compound having an absorption maximum at 352 mμ. Borneol and isoborneol have opposite signs of rotation at the sodium D-line, but both compounds exhibit positive plain dispersion curves of low rotation. The methyl xanthates (XXIX and XXXIII) have on the other hand distinctly different rotatory dispersion curves with quite large rotations.

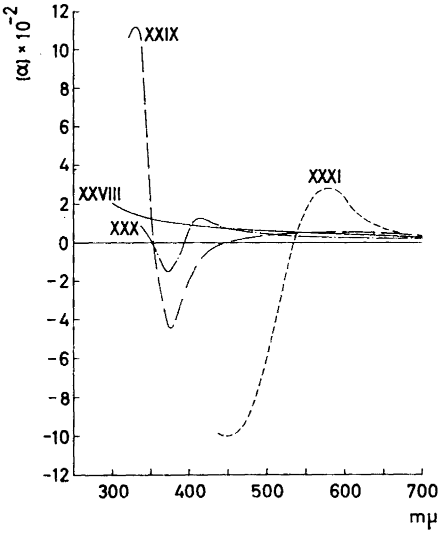


Fig. 11. Optical rotatory dispersion curves of (+)-borneol (XXVIII), methyl bornyl xanthate (XXIX), trityl bornyl xanthate (XXX) and bornyl N-phenyl-N-thiobenzoyl-thiourethane (XXXI).

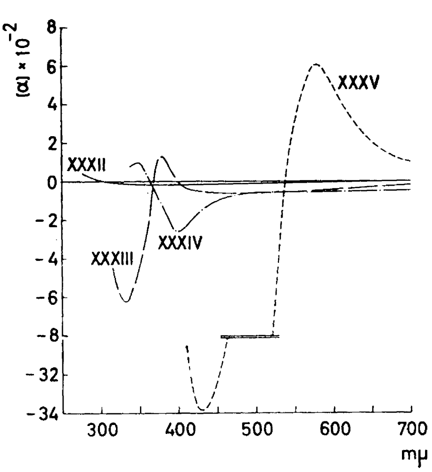
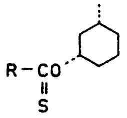


Fig. 12. Optical rotatory dispersion curves of (−)-isoborneol (XXXII), methyl isobornyl xanthate (XXXIII), trityl isobornyl xanthate (XXXIV) and isobornyl N-phenyl-N-thiobenzolthiourethane (XXXV).

The trityl xanthates of cholestan-3β-ol and of *cis*- and *trans*-3-methylcyclohexanol have Cotton effects with larger amplitudes and of opposite sign than those of the corresponding methyl xanthates. The trityl xanthates of borneol (XXX) and isoborneol (XXXIV) exhibit on the contrary Cotton effects of somewhat smaller amplitudes than the methyl xanthates. The rotatory dispersion curve of bornyl trityl xanthate (Fig. 11) has a flat extremum at 425 mμ and a trough at 380 mμ. The Cotton effect must, however, be negative as the absorption maximum is found at 356 mμ, and the peak which should be situated around 325 mμ is not quite resolved. Isobornyl trityl xanthate shows a dispersion curve (Fig. 12) with a negative Cotton effect centered around the 366 mμ absorption band. In the bornyl series the methyl and trityl xanthates have thus the same sign of their Cotton effects whereas they have opposite signs in the isobornyl series. The N-phenyl-N-thiobenzoylthiourethane of borneol (XXXI) as well as that of isoborneol (XXXV) exhibit positive Cotton effects.

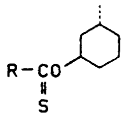
Willard and Pacsu[23] recently prepared benzyl xanthates of a few α-D-glucopyranosides, and we have recorded the optical rotatory dispersion curves of methyl α-D-glucopyranoside-6-(S-benzyl) xanthate (XXXVI) and methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside-6-(S-benzyl) xanthate (XXXVII). These compounds which were kindly supplied by Professor Pacsu (Princeton University), have as expected an absorption band at about 355 mμ of low extinction which evidently is associated with the negative Cotton effects found in their dispersion curves (Fig. 13).



XVI $R = CH_3S$

XVII $R = (C_6H_5)_3CS$

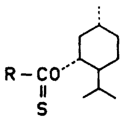
XVIII $R = C_6H_5\underset{\underset{S}{\|}}{C}-\underset{\underset{C_6H_5}{|}}{N}$



XIX $R = CH_3S$

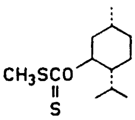
XX $R = (C_6H_5)_3CS$

XXI $R = C_6H_5\underset{\underset{S}{\|}}{C}-\underset{\underset{C_6H_5}{|}}{N}$

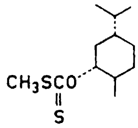


XXII $R = CH_3S$

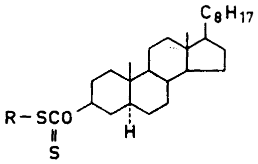
XXIII $R = C_6H_5\underset{\underset{S}{\|}}{C}-\underset{\underset{C_6H_5}{|}}{N}$



XXIV

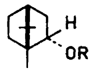


XXV



XXVI $R = CH_3$

XXVII $R = (C_6H_5)_3C$

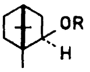


XXVIII $R = H$

XXIX $R = CH_3\overset{\overset{S}{\|}}{S C}$

XXX $R = (C_6H_5)_3CS\overset{\overset{S}{\|}}{C}$

XXXI $R = C_6H_5\overset{\overset{S}{\|}}{C}-\underset{\underset{C_6H_5}{|}}{N}-\overset{\overset{S}{\|}}{C}$



XXXII $R = H$

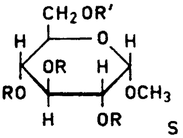
XXXIII $R = CH_3S\overset{\overset{S}{\|}}{C}$

XXXIV $R = (C_6H_5)_3CS\overset{\overset{S}{\|}}{C}$

XXXV $R = C_6H_5\overset{\overset{S}{\|}}{C}-\underset{\underset{C_6H_5}{|}}{N}-\overset{\overset{S}{\|}}{C}$

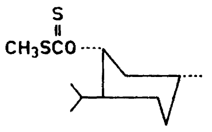
CONCLUSION

The spectroscopic properties of xanthates with absorption bands around 355 mμ and 275 mμ make them very desirable chromophoric derivatives for anomalous rotatory dispersion measurements among the "transparent" alcohols. The 355 mμ band possesses low extinction (log ε ~ 1.6) thus allowing rotatory dispersion measurements through this absorption band. The second band has a strong absorption (log ε ~ 4.2), but the two bands are well separated and the 275 mμ absorption will usually not interfere with spectropolarimetric studies in the 355 mμ absorption region. The strong absorption maximum may also prove useful in analytical applications.

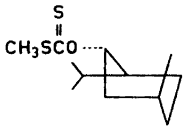


XXXVI $R = H;\ R' = C_6H_5CH_2S\overset{\overset{S}{\|}}{C}$

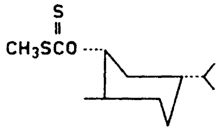
XXXVII $R = C_6H_5\overset{\overset{O}{\|}}{C};\ R' = C_6H_5CH_2S\overset{\overset{S}{\|}}{C}$



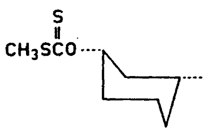
XXXVIII



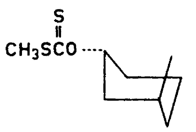
XXXIX



XL



XLI



XLII

The Cotton effect of xanthates will be due to interaction of the partially unshielded nuclei of various substituents with the electrons of the $-\overset{\overset{S}{\|}}{C}-S-$ chromophore. The extent of this interaction depends upon their relative spatial situations, and in view of the free rotation of the xanthate grouping one will observe the effect of an overall rotomer composition. The reason why methyl and trityl xanthates behave differently is that in several instances the large trityl xanthate group may favor a different rotomer composition than the methyl xanthate.

The possibility of free rotation of the xanthate group complicates the situation to such an extent that at the present time a type of "octant rule"[24] approach can not be employed. However, the xanthates can be used for

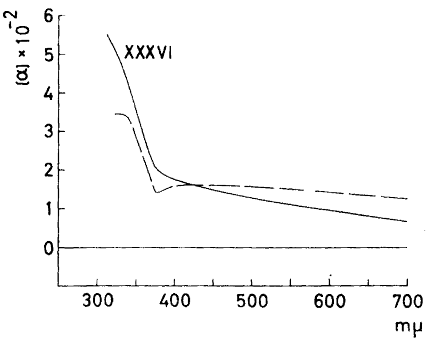


Fig. 13. Optical rotatory dispersion curves of methyl α-D-glucopyranoside-6-(S-benzyl) xanthate (XXXVI) ——— and methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside-6-(S-benzyl) xanthate (XXXVII) — — —.

stereochemical correlations in closely related series of alcohols (*e.g.*, the alcohols corresponding to the compounds V to XIII), and these derivatives offer excellent means of differentiating between steroid α- and β-ols.

The relative configurations of alcohols and their corresponding amines can also be readily established through the rotatory dispersion curves of the xanthate and dithiocarbamate derivatives. The Cotton effects of xanthates will be centered around 355 mμ and those of dithiocarbamates near 330 mμ, and compounds of the same configurations will exhibit Cotton effects of the same sign.

A comparison of the stereochemistry and rotatory dispersion curves of the compounds III to XIII suggests that the configuration of secondary alcohols may be derived directly from the sign of the Cotton effect of their methyl xanthates in the following way: A model of the methyl xanthate is placed similarly as in the Cahn-Ingold-Prelog R and S convention[26], so that the asymmetric carbon atom is in the center of a "steering wheel", the hydrogen below, the xanthate group and the other two substituents on the wheel. When the groups are arranged clockwise in the order xanthate, large (L) and medium (M) the substance will exhibit a positive Cotton effect, and when the groups are arranged counter clockwise the methyl xanthate will have a negative one.

The situation is more complicated when the xanthate group is situated in a cyclic system, as not only free rotation around the C—O bond is possible but also conformational flipping of one chair form into the other when one of the substituents is axial. The ring conformer composition of various alkyl-substituted cyclohexyl acetates have been derived from rate studies of alkaline hydrolysis and spectroscopic investigations [25]. It is likely that methyl xanthates can be studied in the same way, but qualitatively the conformation of methyl xanthates ought to be obtained simply by equating the methyl xanthate group with an acetate group. From the results of Chapman *et al.* [25] it can then be concluded that menthyl methyl xanthate (XXII) will exist entirely as conformation (XXXVIII) with all three groups equatorial. Isomenthyl methyl xanthate (XXIV) ought to be represented mainly by conformation (XXXIX) with the two larger groups equatorial and the smaller methyl group axial, while carvomenthyl xanthate (XXV) will have all three substituents equatorial (XL). It can be seen that the conformational situation around the xanthate grouping is very similar in all three substances with the exception of the relatively distant (from the C=S chromophore) C—3 substituent. Stereochemically, XXXVIII and XL are identical and exhibit identical signs of their Cotton effects. In XXXIX an antipodal relationship exists around the xanthate grouping, thus explaining the inversion in sign in going from XXXVIII to XXXIX.

A similar explanation can be offered for the observation (Figs. 7 and 8) that the 3-methylcyclohexanol derivatives XVI and XIX, though antipodal at the asymmetric center carrying the xanthate grouping, exhibit Cotton effect curves of identical sign and weak amplitude. If we assume again that the relatively distant 3-methyl substituent has only a small effect as far as the C=S chromophore is concerned, then it will be noted that in terms of their preferred conformations [25], XLI and XLII, the immediate asymmetric environment around the xanthate grouping in both *cis*- (XVI) and *trans*- (XIX) alcohols *is identical.* The low amplitude of the Cotton effects of these two substances (as well as of the xanthate of cholestan-3β-ol, XXVI) is also understandable, since nuclear substituents are absent in the immediate vicinity of the xanthate function — the principal interaction responsible for the rotation being with the adjacent ring methylene carbons. In the terpene examples, the increased amplitude of the Cotton effect is undoubtedly associated with the presence of an extra-nuclear substituent in relatively close proximity to the electron cloud of the C=S chromophore.

The rotatory dispersion behavior of the 2-methylcyclohexanol xanthates (XIV, XV) cannot be explained in as simple terms, because one of them, the *cis*-isomer, XIV, consists of a mixture of conformers [25] each of which may also have a different rotomer composition as far as free rotation around the $O-C_1$ bond is concerned.

For stereochemical purposes it seems to be better to study methyl xanthates rather then trityl xanthates or N-phenyl-N-thiobenzoylthiourethanes. From a synthetic standpoint the two xanthates are equally easily prepared and are to be preferred to N-phenyl-N-thiobenzoylthiourethanes. However, the recording of the rotatory dispersion curves of N-phenyl-N-thiobenzoylthiourethanes is facilitated as the Cotton effects are found in the visible spectral range and the amplitudes seem to be quite large.

EXPERIMENTAL

All xanthates were prepared by reacting the alcohols in benzene with sodium dispersion and carbon disulfide. When more than one derivative had to be prepared of an alcohol the sodium xanthate was first isolated and then treated with the appropriate halides. N-Phenyl-N-thiobenzoylthiourethanes were obtained from sodium xanthates and diphenylimine chloride [27,28]. The general procedures are given below in the preparation of methyl L-1-phenyl-2,2-diphenylethyl xanthate (III) and the three derivatives XVI—XVIII of *cis*-3-methylcyclohexanol.

The derivatives were filtered in hexane or benzene solution through alumina, and solid compounds were further purified by recrystallization. In case the derivatives were oils they were subjected to vacuum distillation. Partial elimination of the xanthate group evidently happened in some cases as indicated by the low sulfur value in the analysis. However, spectroscopic data showed that the main part was the desired xanthate (in infrared two strong bands at 8.1—8.2 and 9.3—9.5 μ, and in ultraviolet a low extinction band at about 355 mμ).

Methyl L-2-methylbutyl xanthate (I). Prepared from L-(—)-2-methylbutanol; colourless oil.

$\lambda_{\max}^{\text{isooctane}}$ 355 and 276 mμ, ε 55 and 10 000. R.D. (Fig. 1) in isooctane; c 0.45: $[\alpha]_{589}$ $+10°$, $[\alpha]_{400}$ $+24°$, $[\alpha]_{310}$ $+85°$.

L-2-Methylbutyl N-phenyl-N-thiobenzoylthiourethane (II). Prepared from sodium L-2-methylbutyl xanthate and diphenylimine chloride; red oil.

$\lambda_{\max}^{\text{isooctane}}$ 510 and 315 mμ; ε 240 and 28 700. R.D. (Fig. 1) in isooctane; c 0.225: $[\alpha]_{589}$ $+5°$, $[\alpha]_{430}$ $+17°$.

Methyl L-*1-phenyl-2,2-diphenylethyl xanthate (III).* To 137 mg (0.5 mmole) of (−)-1-phenyl-2,2-diphenylethanol [29] in 50 ml of dry benzene was added 50 mg of a 50 % sodium dispersion, the mixture was heated under reflux overnight, 100 mg of carbon disulfide was added and heating continued for 5 h, and finally 1 ml of methyl iodide was added and the mixture heated with stirring for a further 5 h period. The benzene was filtered, evaporated and the residue dissolved in hexane and filtered through neutral alumina. The hexane was evaporated *in vacuo* and the residue recrystallized from dilute methanol yielding 130 mg; m.p. 122−124°. (Found: C 72.78; H 5.70; S 17.39. Calc. for $C_{22}H_{20}OS_2$: C 72.48; H 5.53; S 17.59).

$\lambda_{\max}^{\text{methanol}}$ 355 and 280 mμ, ε 65 and 10 200. R.D. (Fig. 2) in methanol; *c* 0.115: $[\alpha]_{589}$ −120°, $[\alpha]_{380}$ −1290°, $[\alpha]_{335}$ +507°, $[\alpha]_{320}$ +146°.

N-Dithiocarbomethoxy L-*1-phenyl-2,2-diphenylethylamine (IV).* A mixture of 136 mg (0.5 mmole) of (−)-1-phenyl-2,2-diphenylethylamine [29], 5 ml of 0.1 N sodium hydroxide and 100 mg of carbon disulfide in 50 ml of water and 10 ml of dioxane was shaken for 5 h at room temperature. 1 ml of methyl iodide was added and the mixture shaken for another 5 h. The product was extracted with ether, the ether solution washed with dilute hydrochloric acid, water and then dried. The ether was evaporated and the residue chromatographed on Merck acid-washed alumina. The product was eluted with hexane-benzene (1 : 1). It was recrystallized from dilute methanol yielding 85 mg; m.p. 95−96°. (Found: C 72.90; H 5.87; N 3.65; S 17.53. Calc. for $C_{22}H_{21}NS_2$: C 72.68; H 5.83; N 3.86; S 17.64).

$\lambda_{\max}^{\text{methanol}}$ 330 and 255 mμ, ε 60 and 11 500. R.D. (Fig. 2) in methanol, *c* 0.224: $[\alpha]_{589}$ −54°, $[\alpha]_{370}$ −164°; *c* 0.112; $[\alpha]_{295}$ +540°.

Methyl L-threo-*3-phenyl-2-butyl xanthate (V).* Prepared from L-(+)-*threo*-3-phenyl-2-butanol [30a]; colourless oil. (Found: C 60.04 H 6.86; S 26.50. Calc. for $C_{12}H_{16}OS_2$: C 59.96; H 6.71; S 26.68).

$\lambda_{\max}^{\text{methanol}}$ 354 mμ, ε 52. R.D. (Fig. 3) in methanol; *c* 0.100: $[\alpha]_{589}$ −35°, $[\alpha]_{370}$ −665°, $[\alpha]_{330}$ +620°, $[\alpha]_{322}$ +420°.

Methyl L-threo-*4-phenyl-3-pentyl xanthate (VI).* Prepared from L-(+)-*threo*-4-phenyl-3-pentanol [30b]; oil. (Found: C 62.67; H 7.47; S 23.88. Calc. for $C_{13}H_{18}OS_2$: C 61.37; H 7.13; S 25.21.

$\lambda_{\max}^{\text{methanol}}$ 354 mμ, ε 47. R.D. (Fig. 3) in methanol; *c* 0.090: $[\alpha]_{589}$ −25°, $[\alpha]_{365}$ −350°, $[\alpha]_{330}$ +165°.

Methyl L-erythro-*1,2-diphenylpropyl xanthate (VII).* Prepared from L-(+)-*erythro*-1,2-diphenylpropanol [31a]; m.p. 63−64°, sublimed at 35°/0.01 mm. (Found: C 67.74; H 6.01; S 21.19. Calc. for $C_{17}H_{19}OS_2$: C 67.51; H 6.00; S 21.23).

$\lambda_{\max}^{\text{methanol}}$ 356 mμ, ε 63. R.D. (Fig. 3) in methanol; *c* 0.073: $[\alpha]_{589}$ −11°, $[\alpha]_{376}$ −614°, $[\alpha]_{337}$ +893°, $[\alpha]_{315}$ +613°.

Methyl L-threo-*3-phenyl-2-pentyl xanthate (VIII).* Prepared from L-(−)-*threo*-3-phenyl-2-pentanol [30b]; oil. (Found: C 61.54; H 7.22; S 24.96. Calc. for $C_{13}H_{18}OS_2$; C 61.37; H 7.13; S 25.21).

$\lambda_{\max}^{\text{methanol}}$ 354 mμ, ε 48. R.D. (Fig. 4) in methanol; *c* 0.115: $[\alpha]_{589}$ −80°, $[\alpha]_{367.5}$ −750°, $[\alpha]_{330}$ +401°, $[\alpha]_{317.5}$ +253°.

Methyl L-threo-*3-cyclohexyl-2-butyl xanthate (IX).* Prepared from L-(+)-*threo*-3-cyclohexyl-2-butanol [31b]; oil. (Found: C 58.90; H 9.35; S 23.94. Calc. for $C_{12}H_{22}OS_2$: C 58.49; H 9.00; S 26.02).

$\lambda_{\max}^{\text{methanol}}$ 355 mμ, ε 40. R.D. (Fig. 4) in methanol; *c* 0.165: $[\alpha]_{589}$ +15°, $[\alpha]_{345}$ −140°, $[\alpha]_{327.5}$ +245°, $[\alpha]_{315}$ +225°.

Methyl L-erythro-*3-phenyl-2-butyl xanthate (X).* Prepared from L-(+)-*erythro*-3-phenyl-2-butanol [30a]; oil.

$\lambda_{\text{infl.}}^{\text{methanol}}$ 355 mμ, ε 20. R.D. (Fig. 5) in methanol; *c* 0.050: $[\alpha]_{589}$ +40°, $[\alpha]_{370}$ +835°, $[\alpha]_{342.5}$ +205°, $[\alpha]_{332.5}$ +1100°.

Methyl L-erythro-*3-phenyl-2-pentyl xanthate (XI).* Prepared from L-(−)-*erythro*-3-phenyl-2-pentanol [30b]; oil. (Found: C 61.67; H 7.21; S 24.81. Calc. for $C_{13}H_{18}OS_2$: C 61.37; H 7.13; S 25.21).

$\lambda_{\max}^{\text{methanol}}$ 354 mμ, ε 58. R.D. (Fig. 5) in methanol: *c* 0.100: $[\alpha]_{589}$ −25°, $[\alpha]_{370}$ +347°, $[\alpha]_{347.5}$ −865°, $[\alpha]_{300}$ −30°.

Methyl erythro-*1,2-di(isopropyl)-2-phenylethyl xanthate (XII).* Prepared from (−)-*erythro*-1,2-di(isopropyl)-2-phenylethanol [32]; m.p. 69−70°, from ligroin. (Found: C 64.77; H 8.20; S 21.16. Calc. for $C_{16}H_{24}OS_2$: C 64.82; H 8.16; S 21.63).

$\lambda_{\max}^{\text{methanol}}$ 355 mμ, ε 68. R.D. (Fig. 5) in methanol; *c* 0.105: $[\alpha]_{589}$ −18°, $[\alpha]_{372.5}$ +275°, $[\alpha]_{320}$ −1030°, $[\alpha]_{307.5}$ −820°.

Methyl erythro-*1,2-diphenyl-2-methylbutyl xanthate (XIII).* Prepared from (+)-*erythro*-1,2-diphenyl-2-methylbutanol [14]; oil. (Found: C 69.21; H 6.55; S 18.79. Calc. for $C_{19}H_{22}OS_2$: C 69.05; H 6.71; S 19.40).

$\lambda_{\text{infl.}}^{\text{methanol}}$ 355 mμ, ε 50. R.D. (Fig. 4) in methanol; *c* 0.105: $[\alpha]_{589}$ −70°, $[\alpha]_{375}$ −655°, $[\alpha]_{330}$ +140°, $[\alpha]_{320}$ +50°.

(+)-cis-*2-Methylcyclohexanol.* This alcohol was prepared according to Gough, Hunter and Kenyon [15]. However, recrystallization of the half phthalate strychnine salt was interrupted before full optical purity had been reached, and an alcohol with a specific rotation of +4.85° (neat) was obtained. The optically pure alcohol has a rotation of +12.46° (neat) [15] and hence the alcohol used in our experiments was 39 % resolved.

Oxidation of the alcohol gave a 2-methylcyclohexanone whose rotatory dispersion curve exhibited a negative Cotton effect.

Methyl (+)-cis-*2-methylcyclohexyl xanthate (XIV).* Prepared from an alcohol with the rotation $[\alpha]_D$ +4.85° (neat); oil. (Found: C 53.69; H 7.74. Calc. for $C_9H_{16}OS_2$: C 52.94; H 7.85).

$\lambda_{\max}^{\text{isooctane}}$ 356 and 276 mμ, ε 46 and 10 300. R.D. (Fig. 6) in isooctane; *c* 0.275: $[\alpha]_{589}$ +11°, $[\alpha]_{375}$ −182°, $[\alpha]_{330}$ +390°, $[\alpha]_{322.5}$ +380°, (these rotations are corrected to 100 % resolution).

trans-*2-Methylcyclohexanol.* The racemic alcohol was prepared according to Gough, Hunter and Kenyon [15], the only difference beeing that commercial 2-methylcyclohexanol (Eastman Kodak, practical) was used.

(+)-trans-*2-Methylcyclohexanol.* This alcohol has previously been prepared by a difficult and tedious method [15]. Partial resolution was readily encountered by recrystallization of the 3β-acetoxy-Δ^5-etienate. 3β-Acetoxy-Δ^5-etienate of racemic *trans*-2-methylcyclohexanol was prepared in a similar way to that described by Djerassi and Staunton [17]. The ester was recrystallized three times from acetone, the ester reduced with lithium aluminium hydride and the partially resolved alcohol was distilled in a hot box at 70°/15 mm. $[\alpha]_D$ +5.27° (neat) as compared to $[\alpha]_D$ +34.38° (neat) for the optically pure alcohol [15]. The sample was thus 15 % resolved.

Oxidation gave a ketone with a positive Cotton effect.

Methyl (+)-trans-*2-methylcyclohexyl xanthate (XV).* Prepared from an alcohol with the rotation $[\alpha]_D$ +5.27 (neat); oil. (Found: C 54.28; H 8.07. Calc. for $C_9H_{16}OS_2$: C 52.94; H 7.85).

$\lambda_{\max}^{\text{isooctane}}$ 356 and 276 mμ, ε 41 and 10 100. R.D. (Fig. 6) in isooctane; *c* 0.500: $[\alpha]_{589}$ + 35°, $[\alpha]_{370}$ −130°, $[\alpha]_{330}$ +985° (these rotations are corrected to 100 % resolution).

(+)-3-Methylcyclohexanone. The ketone was prepared from pulegone according to McElvain and Eisenbraun [19].

(−)-cis-*3-Methylcyclohexanol.* The optically pure alcohol was prepared according to Hückel and Kurz [18]. However, (+)-3-methylcyclohexanone was reduced with lithium aluminium hydride instead of sodium in alcohol which improved the yield. $[\alpha]_D$ −3.90° (neat). Hückel and Kurz reported $[\alpha]_D^{20}$ −3.91° (neat).

Sodium cis-*3-methylcyclohexyl xanthate.* To 3.2 g (0.028 mole) of (−)-*cis*-3-methylcyclohexanol in 75 ml of dry benzene was added 1.4 g of 50 % sodium dispersion (0.03 gatom), the reaction mixture was stirred for one hour at room temperature and 5 ml of carbon disulfide was added. The mixture was stirred overnight, ether added and the product filtered. The sodium xanthate was recrystallized from benzene-ether, yielding 4.8 g; m.p. 200°(decomp.).

Methyl cis-*3-methylcyclohexyl xanthate (XVI).* To 0.85 g of the sodium xanthate in a mixture of 50 ml of benzene and 25 ml of acetone was added 5 ml of methyl iodide. The reaction mixture was stirred for 24 h at room temperature, filtered and the solvent evaporated *in vacuo*. The residue was dissolved in benzene and filtered through Merck acid-washed alumina, the benzene evaporated and the xanthate distilled at a bath temperature of 80°/0.2 mm. (Found C 52.85; H 7.61; S 31.22. Calc. for $C_9H_{16}OS_2$: C 52.94; H 7.85; S 31.40).

$\lambda_{\max}^{\text{isooctane}}$ 355 and 276 mμ, ε 45 and 10 700. R.D. (Fig. 7) in isooctane; c 0.193: $[\alpha]_{589}$ −45°, $[\alpha]_{360}$ −175°, $[\alpha]_{335}$ −160°, $[\alpha]_{315}$ −235°.

Trityl cis-*3-methylcyclohexyl xanthate (XVII).* A mixture of 420 mg of sodium *cis*-3-methylcyclohexyl xanthate and 650 mg of trityl bromide in 100 ml of benzene was stirred for 24 h at room temperature, filtered and the solvent evaporated. The residue was dissolved in benzene and filtered through Merck acid-washed alumina. The product was recrystallized from acetone-water and 650 mg was obtained; m.p. 142−143°. (Found: C 74.54; H 6.10; S 14.71. Calc. for $C_{27}H_{28}OS_2$: C 74.96; H 6.52; S 14.82).

$\lambda_{\max}^{\text{dioxane}}$ 366 and 295 mμ, ε 80 and 11 100. R.D. (Fig. 7). in dioxane; c 0.142: $[\alpha]_{589}$ −10°, $[\alpha]_{410}$ −36°, $[\alpha]_{377.5}$ −15°, $[\alpha]_{340}$ −132°, $[\alpha]_{330}$ −100°.

cis-*3-Methylcyclohexyl N-phenyl-N-thiobenzoylthiourethane (XVIII).* A mixture of 420 mg of sodium *cis*-3-methylcyclohexyl xanthate and 440 mg of diphenylimin chloride [33] in 100 ml of dry benzene was stirred at room temperature for 24 h. The mixture was filtered, concentrated and chromatographed on Merck acid-washed alumina. The product was eluted with benzene to yield 575 mg of red crystals. After one recrystallization from hexane there remained 500 mg of red flat plates: m.p. 121−122.5°. (Found C 68.13; H 6.11; N 3.60; S 17.63. Calc. for $C_{21}H_{23}NOS_2$: C 68.22; H 6.28; N 3.79; S 17.35).

$\lambda_{\max}^{\text{dioxane}}$ 512 and 315 mμ, ε 165 and 8750. R.D. (Fig. 7) in dioxane; c 0.140: $[\alpha]_{589}$ +90°, $[\alpha]_{580}$ +95°, $[\alpha]_{467.5}$ −335°, $[\alpha]_{430}$ −300°.

(−)-trans-*3-Methylcyclohexanol.* Prepared according to Hückel and Kurz [18]. $[\alpha]_D$ −7.35° (neat). Hückel and Kurz reported $[\alpha]_D^{20}$ −7.34° (neat).

Methyl trans-*3-methylcyclohexyl xanthate (XIX).* Prepared in the same way as the corresponding *cis*-derivative; oil. (Found: C 52.58; H 7.77; S 31.12. Calc. for $C_9H_{16}OS_2$: C 52.94; H 7.85; S 31.40).

$\lambda_{\max}^{\text{isooctane}}$ 354 and 276 mμ, ε 43 and 10 700. R.D. (Fig. 8) in isooctane; c 0.119: $[\alpha]_{589}$ −18°, $[\alpha]_{410}$ −35°, $[\alpha]_{377.5}$ −11°, $[\alpha]_{340}$ −89°, $[\alpha]_{315}$ −29°.

Trityl trans-*3-methylcyclohexyl xanthate (XX).* Prepared in the same way as the corresponding *cis*-derivative; m.p. 133−135°, from acetone-water. (Found: C 74.50; H 6.20; S 14.53. Calc. for $C_{27}H_{28}OS_2$: C 74.96; H 6.52; S 14.82).

$\lambda_{\max}^{\text{dioxane}}$ 370 and 295 mμ, ε 80 and 10 700. R.D. (Fig. 8) in dioxane; c 0.190: $[\alpha]_{589}$ +5°, $[\alpha]_{402.5}$ +125°, $[\alpha]_{352.5}$ −145°, $[\alpha]_{340}$ −130°.

trans-*3-Methylcyclohexyl N-phenyl-N-thiobenzoylthiourethane (XXI).* Prepared in the same way as the corresponding *cis*-derivative; m.p. 98−99°, from hexane.(Found:C 67.74; H 6.30; N 3.70; S 16.94. Calc. for $C_{21}H_{23}NOS_2$: C 68.22; H 6.28; N 3.79; S 17.35).

$\lambda_{\max}^{\text{dioxane}}$ 509 and 317 mμ, ε 161 and 8 700. R.D. (Fig. 8) in dioxane; c 0.056: $[\alpha]_{589}$ +320°, $[\alpha]_{577.5}$ +325°, $[\alpha]_{460}$ −1150°, $[\alpha]_{437.5}$ −1125°.

Methyl menthyl xanthate (XXII). Prepared from (−)-menthol; oil.

$\lambda_{\max}^{\text{isooctane}}$ 356 and 276 mμ, ε 44 and 10 850. R.D. (Fig. 9) in isooctane; c 0.185: $[\alpha]_{589}$ −69°, $[\alpha]_{375}$ +934°; c 0.093: $[\alpha]_{327.5}$ −2370°, $[\alpha]_{305}$ −1935°.

Menthyl N-phenyl-N-thiobenzoylthiourethane (XXIII). Prepared according to Tschugaeff [27]; m.p. 104−106°, from petroleum ether.

$\lambda_{\max}^{\text{isooctane}}$ 512 and 315 mμ, ε 120 and 8 100. R.D. (Fig. 9) in isooctane; c 0.112: $[\alpha]_{589}$ −502°, $[\alpha]_{565}$ −667°, $[\alpha]_{455}$ +1575°, $[\alpha]_{440}$ +1560°.

Methyl isomenthyl xanthate (XXIV). Prepared from (+)-isomenthol [20]; oil. (Found: C 58.89; H 9.02; S 22.42. Calc. for $C_{12}H_{22}OS_2$; C 58.48; H 9.00; S 26.03).

$\lambda_{\max}^{\text{isooctane}}$ 354 and 276 mμ, ε 44 and 11 900. R.D. (Fig. 9) in isooctane; c 0.150: $[\alpha]_{589}$ +9°, $[\alpha]_{372.5}$ −387°, $[\alpha]_{330}$ +584°, $[\alpha]_{320}$ +550°.

Methyl carvomenthyl xanthate (*XXV*). Prepared from (−)-carvomenthol; oil. (Found: C 58.00; H 8.90; S 23.80. Calc. for $C_{12}H_{22}OS_2$: C 58.48; H 9.00; S 26.03).

$\lambda_{\max}^{\text{isooctane}}$ 354 and 276 mμ, ε 44 and 11 900. R.D. (Fig. 9) in isooctane; c 0.115: $[\alpha]_{589}$ −107°, $[\alpha]_{425}$ −200°, $[\alpha]_{377.5}$ +294°, $[\alpha]_{325}$ −1840°, $[\alpha]_{317.5}$ −1780°.

Methyl β-cholestanyl xanthate (XXVI). The compound was prepared essentially according to O'Conner and Nace [35], but the sodium xanthate was isolated and then reacted with methyl iodide; m.p. 87–88°, from acetone. O'Conner and Nace reported 87.5–88°.

$\lambda_{max}^{isooctane}$ 356 and 276 mμ, ε 51 and 16 100. R.D. (Fig. 10) in isooctane; *c* 0.441: $[\alpha]_{589}$ +9°, $[\alpha]_{370}$ −40°, $[\alpha]_{340}$ +35°, $[\alpha]_{335}$ −50°.

Trityl β-cholestanyl xanthate (XXVII). Prepared from the sodium xanthate and trityl bromide; m.p. 164–166°, from acetone. (Found: C 79.14; H 8.55; S 9.48. Calc. for $C_{46}H_{59}OS_2$: C 79.77; H 8.74; S 9.20).

$\lambda_{max}^{dioxane}$ 356 and 285 mμ, ε 100 and 14 600. R.D. (Fig. 10) in dioxane; *c* 0.210: $[\alpha]_{589}$ +12°, $[\alpha]_{375}$ +45°, $[\alpha]_{335}$ −84°, $[\alpha]_{325}$ −57°.

(+)-Borneol (XXVIII). Camphor was reduced with sodium in dilute ethanol and the borneol purified by repeated recrystallization of its half phthalate from acetic acid and hexane to m.p. 163–164°. The borneol was recrystallized from petroleum ether; m.p. 205–206°, $[\alpha]_D$ +37.1° in chloroform.

Methyl bornyl xanthate (XXIX). From sodium bornyl xanthate and methyl iodide; m.p. 51.5–52°, from dilute methanol. Tschugaeff [10a] reported m.p. 51–52°.

$\lambda_{max}^{isooctane}$ 356 and 274 mμ, ε 42 and 17 700. R.D. (Fig. 11) in isooctane; *c* 0.105: $[\alpha]_{589}$ + 55° $[\alpha]_{380}$ −430°, $[\alpha]_{330}$ +1125°, $[\alpha]_{320}$ + 1060°.

Trityl bornyl xanthate (XXX). From sodium bornyl xanthate and trityl bromide; m.p. 144–146°, from petroleum ether. Tschugaeff [10b] reported 144–146°.

$\lambda_{max}^{dioxane}$ 356 and 297 mμ, ε 38 and 11 000. R.D. (Fig. 11) in dioxane; *c* 0.275: $[\alpha]_{589}$ +35°, $[\alpha]_{415}$ +120° $[\alpha]_{370}$ −147°, $[\alpha]_{335}$ +90°.

Bornyl N-phenyl-N-thiobenzoylthiouretane (XXXI). From sodium bornyl xanthate and diphenylimine chloride; red oil. (Found: C 69.09; H 6.42; S 15.81. Calc. for $C_{24}H_{27}NOS_2$: C 70.37; H 6.64; S 15.66).

$\lambda_{max}^{dioxane}$ 512 and 315 mμ, ε 172 and 17 050. R.D. (Fig. 11) in dioxane; *c* 0.135: $[\alpha]_{589}$ +260°, $[\alpha]_{575}$ +280°; *c* 0.027: $[\alpha]_{450}$ −990°, $[\alpha]_{430}$ −985°.

(−)-Isoborneol (XXXII). Camphor was hydrogenated using Raney nickel as catalyst and the isoborneol was purified by repeated recrystallization of its half phthalate. The alcohol was further purified by recrystallization from petroleum ether and sublimation; m.p. 213–213.5°, $[\alpha]_D$ −29.7° in chloroform. Asahina [34] reported; m.p. 214°, $[\alpha]_D$ −30.6° in ethanol.

Methyl isobornyl xanthate (XXXIII). Prepared in the same way as the corresponding bornyl derivative; oil. (Found: C 60.89; H 8.29; S 24.52. Calc. for $C_{12}H_{20}OS_2$: C 58.97; H 8.25; S 26.24).

$\lambda_{max}^{isooctane}$ 352 and 275 mμ, ε 215 and 17 200. R.D. (Fig. 12) in isooctane; *c* 0.282: $[\alpha]_{589}$ −48°, $[\alpha]_{470}$ −68°; *c* 0.141: $[\alpha]_{377.5}$ +125°, $[\alpha]_{330}$ −625°, $[\alpha]_{315}$ −460°.

Trityl isobornyl xanthate (XXXIV). Prepared in the same way as the corresponding bornyl derivative; m.p. 134–136°, from petroleum ether. Lowry and Hudson [11] reported 134–136°.

$\lambda_{max}^{dioxane}$ 366 and 296 mμ, ε 35 and 14 700. R.D. (Fig. 12) in dioxane; *c* 0.095: $[\alpha]_{589}$ −45°, $[\alpha]_{400}$ −262°, $[\alpha]_{345}$ +95°, $[\alpha]_{335}$ +75°.

Isobornyl N-phenyl-N-thiobenzoylthiouretane (XXXV). Prepared in the same way as the corresponding bornyl derivative: red oil. (Found: S 15.43. Calc for. $C_{27}H_{25}NOS_2$: S 15.66).

$\lambda_{max}^{dioxane}$ 510 and 315 mμ, ε 256 and 30 600. R.D. (Fig. 12) in dioxane; *c* 0.128: $[\alpha]_{589}$ +525°, $[\alpha]_{575}$ +600°, $[\alpha]_{430}$ −3380°, $[\alpha]_{410}$ −3050°.

Methyl α-D-glucopyranoside-6-(S-benzyl) xanthate (XXXVI). Sample [23] supplied by Prof. Pacsu.

$\lambda_{max}^{dioxane}$ 354 and 281 mμ, ε 62 and 11 900. R.D. (Fig. 13) in dioxane; *c* 0.107: $[\alpha]_{589}$ +80°, $[\alpha]_{375}$ +204°, $[\alpha]_{335}$ +443°, $[\alpha]_{315}$ +555°.

Methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside-6-(S-benzyl) xanthate (XXXVII). Sample [23] supplied by Prof. Pacsu.

$\lambda_{max}^{dioxane}$ 355 and 281 mμ, ε 83 and 13 700. R.D. (Fig. 13) in dioxane; *c* 0.118: $[\alpha]_{589}$ +123°, $[\alpha]_{377.5}$ +143°, $[\alpha]_{330}$ +345°, $[\alpha]_{315}$ +343°.

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