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Products of the Determination of the Iodine Value with Iodine Monobromide

The iodine value (iodine number) is an important analytical characteristic of fats and oils. Leading pharmacopeias determine it using iodine monobromide (Hanuš method). We used methyl oleate as a simple analog of unsaturated triacylglycerols to identify the products. After performing the reaction in deuterated solvents under pharmacopeial conditions, NMR spectroscopy revealed the presence of the 9,10-diiodo, 9,10-dibromo, and 9,10-bromoiodo adducts, leaving no educt olefin. The prescribed subsequent addition of potassium iodide led to the formation of methyl 9,10-diiodo and bromoiodo stearate in equal amounts.

Keywords: Iodine value; Fats; Hanuš method; Pharmacopeia; Iodine monobromide

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Introduction

The iodine value (syn. iodine number) is a measure of unsaturation of an organic compound obtained by determining the amount of iodine absorbed over a specific period of time. It is a very important assay for the characterization of fats and (fixed) oils, both in food and pharmaceutical analysis [1–3]. The European (Ph. Eur.) [4], Japanese [5], and United States Pharmacopeia (USP) [6] define it as the number of grams of iodine absorbed, under the prescribed conditions, by 100 g of the substance. For the actual determination, pharmacopeias do not use iodine. The Japanese Pharmacopeia uses a mixture of iodine and iodine trichloride in acetic acid (Wijs method). The European and United States Pharmacopeias specify iodine monobromide. This is the method according to Hanuš [7], the reaction taking place in a mixture of acetic acid and chloroform. After a specified time for the addition of the interhalogen compound to the double bonds, potassium iodide solution is added. This reacts with excess IBr to form I_2 which is titrated with sodium thiosulfate. It is considered as a conventional method, requiring an exact reproduction of a standardized protocol.

In spite of the importance of this method, surprisingly the products of the two reaction steps are not known with certainty. Reaction of IBr with olefins may give bromoiodo, dibromo, and diiodo alkanes. The latter may partly result from the disproportionation of IBr to Br_2 and I_2. In CCl_4 solution, the degree of dissociation of IBr was reported to be approx. 8 % [8]. In contrast to propositions in some textbooks and papers, I_2 reacts smoothly with olefins [9, 10]. The relative rates of addition of Br_2, IBr, and ICl to cyclohexene were determined [11], with the most polar halogen (ICl) adding fastest, the least polar (Br_2) adding slowest. The reactivity differences were small, however: in all cases in acetic acid the reaction went to approx. 90 % completion within a few minutes.

The composition of the product mixture may further be influenced by substitution reactions, especially of bromide by iodide. The occurrence of substitutions was suspected, but not proven [12]. Substitution would be expected for the second step, the addition of the iodide solution. Iodide is also known [13] to trigger the elimination of halogen from 1,2-dihaloalkanes which would regenerate the original alkenes. The lower the pH, the faster the elimination [11].

Back in 1925/26, Holde and Gorgas reported on the reaction products of IBr with erucic and linoleic acid [14]. They isolated 74–97 % of bromoiodobehenic acid ($C_{22}H_{42}BrIO_2$) and dibromodiiodostearic acid ($C_{18}H_{32}Br_2I_2O_2$). They did not report the isolation of dibromo adducts; reaction conditions are not specified; structure elucidation was done by combustion analysis and determination of the molecular masses through titration. These findings are in contradiction to a later Japanese paper [15] on the reaction products of oleic and linoleic acids with IBr. They observed the bromine adducts only. Again, the reaction was not performed under pharmacopeial conditions, and they used a purification and detection procedure that may easily have led to artifacts of the actual reaction products.

In order to clarify this situation, we chose to run the addition of IBr under the conditions prescribed by Ph. Eur.

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Note

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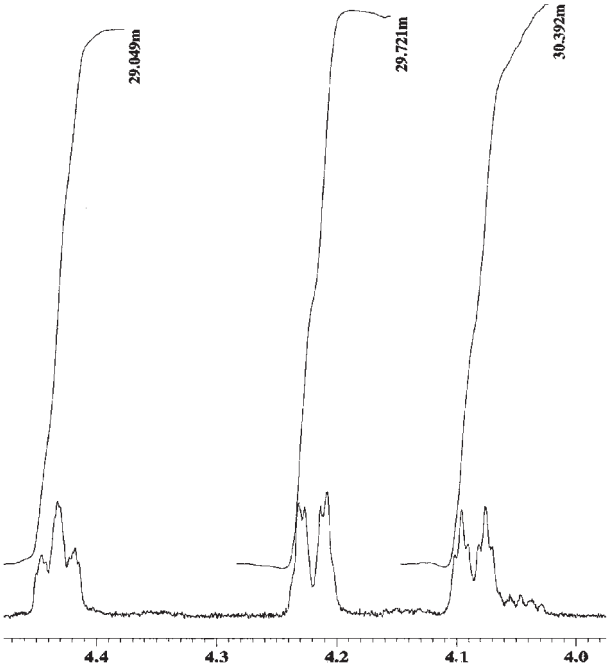
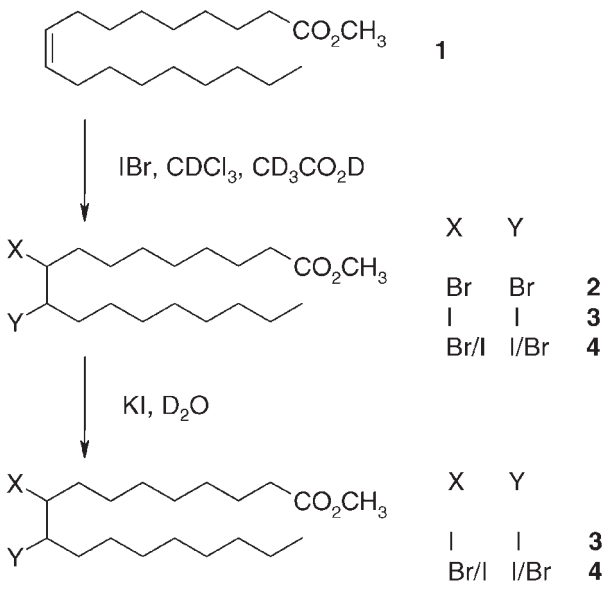


Figure. Section of ^{1}H NMR spectrum of **2**, **3**, and **4** showing the signals of the –CHX–CHY– moieties.



Scheme. Reaction of IBr with methyl oleate under pharmacopeial conditions in deuterated solvents.

2002, using methyl oleate as a model compound of fats and fixed oils. We performed the reaction in deuterated solvents ($CDCl_3$, CD_3COOD, D_2O) and recorded NMR spectra at the specified times so as to analyze the primary product composition without interference through workup.

Results and discussion

After the time specified in both the USP and Ph. Eur. for the addition reaction, ^{1}H NMR revealed complete transformation of methyl oleate **1** to three products with almost equal integrals (Figure and Scheme). The olefinic peak at 5.31 ppm had vanished; instead, there were three multiplets at 4.44, 4.22, and 4.08 ppm. The exact integral ratio was 1 : 1.02 : 1.04. We compared the chemical shifts and fine structures of the –CHX–CHY– moieties with literature data. They could be assigned to the 9-H and 10-H of 9,10-dibromo [16], 9,10-diiodo [10], and 9/10-bromoiodo methyl stearates **2**, **3**, and **4**. The former (**2** and **3**) gave double doublets of the kind expected from the stereospecific addition to a *cis* double bond ([16], Fig. 3 a), the latter (**4**) a double triplet typical of a –CHX–CHY– moiety of respective stereochemistry ([16], Fig. 4 a). The ^{13}C NMR spectrum showed the expected number of six C–X signals; see Experimental Section. Both ^{1}H and ^{13}C NMR showed no further reaction products. The next step – addition of aqueous KI solution – again was performed according to Ph. Eur. 2002, using D_2O instead of water. The resulting organic phase was separated and analyzed by NMR. The peak of methyl 9,10-dibromostearate at 4.22 ppm had vanished, leaving only the signals of the diiodo and bromoiodo ester (**3** and **4**) at 4.40 and 4.07 ppm in approx. equimolar amount (integral ratio, 1.03 : 1). (A trace of the dibromostearate may still have been present, but could not be detected by NMR.) This substitution occurred immediately and was finished after approx. 30 min, no further substitution of bromide by iodide being detectable under these conditions. Since the pharmacopeias specify no waiting time between the addition of KI and the start of the titration, it will take place parallel to the latter process, but should not have any influence on it because there is a large excess of iodide ions.

Conclusions

With methyl oleate, the reaction of IBr goes to completion within the time specified by pharmacopeias. The subsequent process after addition of KI also proceeds quickly, leading to two products only. Since the double bonds in acyl residues of natural fats are isolated, they should react independently of each other, implying a comparable rate of addition of IBr. The elucidation of the clear-cut, fast performance of this reagent explains the good reproducibility and usefulness of the Hanuš method. Our study shows that under pharmacopeial conditions, IBr and olefins neither form just bromoiodo [14] nor just dibromo adducts [15], but dibromo, bromoiodo, and also diiodo alkanes.

Experimental section

Methyl oleate (p.a. standard for GC) was purchased from Fluka company, Switzerland; chloroform D_1 (>99.8 % D), acetic acid D_4 (>99.5 % D), IBr (>98 %) and KI (>99.5 %) from Merck KGaA, Germany; D_2O (>99.9 % D) from Aldrich GmbH, Germany.

The solutions, reaction conditions, and times were as described in Ph. Eur. 2002 [4]. IBr (0.200 g; 0.967 mmol) was dissolved in CD_3CO_2D to give 10.00 mL solution. KI (10.000 g; 60.241 mmol) was dissolved in D_2O to give 100.00 mL solution. Methyl oleate (0.0125 g; 0.0422 mmol) was dissolved in 0.75 mL of $CDCl_3$. 1.25 mL of the IBr solution was added and the mixture kept in the dark for 30 min, shaking frequently, and immediately submitted to NMR analysis. For the determination of the products after addition of KI, this mixture was treated with 0.5 mL of the KI solution and 5.00 mL of D_2O and kept in the dark for 45 min. The organic layer was immediately submitted to NMR analysis.

NMR spectra were run on a Jeol Delta 500 spectrometer at 22.1 °C with a frequency of 500.159 MHz and a frequency range of 7.507 kHz.

(1) Product of the reaction of IBr and methyl oleate: ^{1}H NMR ($CDCl_3$, CD_3CO_2D): δ (ppm) 4.43 (broad triplet, ^1J = 6.6 Hz, 2 H, 9/10-H of methyl diiodostearate), 4.23 (broad double doublet, ^1J = 9.4 and 2.8 Hz, 2 H, 9/10-H of methyl dibromostearate), 4.08 (broad double triplett, ^1J = 9.9 and 3.2 Hz, 2 H, 9/10-H of methyl bromoiodostearate), 3.65 (singlet, 3 H, OCH_3), 2.31 (triplet, ^1J = 7.3 Hz, 2-CH_2), 1.84 (multiplet, 2 H, 3-CH_2), 1.59 (multiplet, 4 H, 8- and 11-CH_2), 1.29 (multiplet, 20 H, remaining CH_2), 0.87 (triplet, ^1J = 6.7 Hz, 18-CH_3). – ^{13}C NMR ($CDCl_3$, CD_3CO_2D): δ (ppm) 171.16 (C=O), 57.06 (CBr), 57.01 (CBr), 55.68 (CBr), 55.63 (CBr), 47.46 (OCH_3), 38.37 (CI), 38.31 (CI), 32.56, 32.32, 31.15, 29.89, 27.83, 20.80, 18.60, 9.74 (CH_3). The remaining signals showed strong overlapping.

(2) Product of the reaction of (1) and aqueous KI: ^{1}H NMR ($CDCl_3$): δ (ppm) 4.39 (multiplet, 2 H, 9/10-H of methyl diiodostearate), 4.07 (broad doublet, 2 H, 9/10-H of methyl bromoiodostearate), 3.64 (singlet, 3 H, OCH_3), 2.28 (triplet, 2 H, ^1J = 7.6 Hz, 2-CH_2), 1.80 (multiplet, 2 H, 3-CH_2), 1.55 (broad multiplet, 4 H, 8- and 11-CH_2), 1.26 (multiplet, 20 H, CH_2), 0.85 (triplet, ^1J = 7.1 Hz, 18-CH_3).

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