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## Synthesis of 3-Glucuronides of Unconjugated and Conjugated Bile Acids<sup>1)</sup>

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The 3-glucuronides of unconjugated, glyco- and tauro-conjugated bile acids have been prepared by an unequivocal route. Among three synthetic routes leading to the desired compounds, a method involving glucuronidation of the p-nitrophenyl ester by means of the Koenigs-Knorr reaction and subsequent conversion of the activated ester into the glyco- and tauro-conjugates was found to be most suitable. The nuclear magnetic resonance spectral data for bile acid glucuronides and related compounds are tabulated.

Keywords—bile acid 3-glucuronide; glycine conjugate; taurine conjugate; glucuronidation; Koenigs-Knorr reaction; cadmium carbonate; p-nitrophenyl ester; activated ester method

In recent years considerable work has been done on the metabolism of bile acids in patients with hepatobiliary diseases.<sup>3,4)</sup> Particular attention has been focused on the physiological significance of sulfation and glucuronidation of bile acids. As a part of series of studies we reported the preparation of bile acid monosulfates<sup>5)</sup> and their separation by high-performance liquid chromatography.<sup>6,7)</sup> Bile acid glucuronides have previously been shown to be present in the urine and plasma of patients with extra- and intrahepatic cholestasis and in trace amounts in the urine of healthy subjects.<sup>8,9)</sup> However, the complete structures of bile acid glucuronides have not definitely been established. Synthetic specimens are therefore required to establish a reliable method for the analysis of bile acid glucuronides in biological fluids in connection with metabolic studies in man. The present paper deals with the preparation of 3-glucuronides of unconjugated, glyco- and tauro-conjugated bile acids by an unequivocal route.

Our initial effort was directed to the synthesis of 3-glucuronides of unconjugated bile acids. Although direct glucuronidation of unconjugated bile acids by means of the Koenigs-Knorr reaction has been reported,  $^{10}$  the structures of the products still remain unclear. Accordingly, methyl lithocholate (2), the 7-monoformate of methyl chenodeoxycholate (13), the 7-monoformate of methyl ursodeoxycholate (22), the 12-monoformate of methyl deoxycholate (32) and the 7,12-diformate of methyl cholate (41), obtainable by reported methods, were taken as starting materials. Introduction of the glucuronyl residue into suitably protected bile acid methyl esters was achieved using the Koenigs-Knorr reaction with methyl 1-bromo-1-deoxy-2,3,4-tri-O-acetyl- $\beta$ -D-glucopyranuronate in anhydrous toluene, employing cadmium carbonate as a catalyst, providing the corresponding glucuronide acetate-methyl esters (4, 15, 24,

<sup>1)</sup> Part CLIV of "Studies on Steroids" by T. Nambara; Part CLIII: M. Numazawa, Y. Kiyono, and T. Nambara, Anal. Biochem., in press. The following trivial names are used in this paper: lithocholic acid= $3\alpha$ -hydroxy- $5\beta$ -cholan-24-oic acid; chenodeoxycholic acid= $3\alpha$ , $7\alpha$ -dihydroxy- $5\beta$ -cholan-24-oic acid; ursodeoxycholic acid= $3\alpha$ , $7\beta$ -dihydroxy- $5\beta$ -cholan-24-oic acid; deoxycholic acid= $3\alpha$ , $12\alpha$ -dihydroxy- $5\beta$ -cholan-24-oic acid; cholic acid= $3\alpha$ , $12\alpha$ -trihydroxy- $12\alpha$ -trihydroxy- $12\alpha$ -cholan-24-oic acid.

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Chart 1. Lithocholate 3-Glucuronide and Related Compounds

COR

HO

HO

HO

COR

G'O

H

OCHO

GO

H

12: R=OH

13: R=OCH<sub>3</sub>

16: R=OC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> (
$$p$$
)

14: R=NHCH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>

17: R=NHCH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>

18: R=NHCH<sub>2</sub>COO<sub>2</sub>H<sub>5</sub>

18: R=NHCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>H

Chart 2. Chenodeoxycholate 3-Glucuronide and Related Compounds

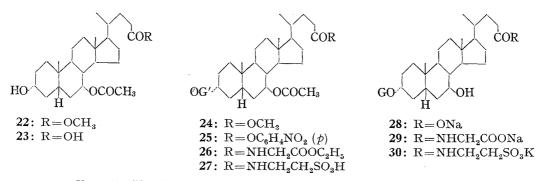


Chart 3. Ursodexycholate 3-Glucuronide and Related Compounds

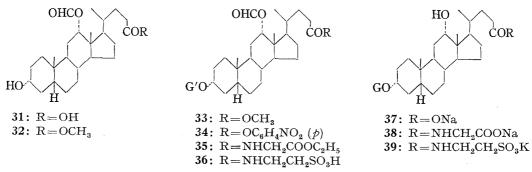


Chart 4. Deoxycholate 3-Glucuronide and Related Compounds

Chart 5. Cholate 3-Glucuronide and Related Compounds

33, 43) in satisfactory yields. Simultaneous removal of the protecting groups in both the steroid and sugar moieties was effected by treatment with methanolic sodium hydroxide to afford the desired 3-glucuronides of unconjugated bile acids (9, 19, 28, 37, 47).

The second project was focused on the synthesis of 3-glucuronides of glyco- and tauro-conjugated bile acids. It has previously been established that the glyco- and tauro-conjugates can be readily obtained from the corresponding p-nitrophenyl ester by treatment with ethyl glycinate or taurine in pyridine.<sup>5)</sup> Accordingly, the preparation of the desired 3-glucuronides of conjugated bile acids was attempted employing three possible procedures. These synthetic routes are different in the sequence of three reactions, glucuronidation at C-3, esterification with p-nitrophenol and amide formation with ethyl glycinate or taurine at C-24.

When ethyl 7,12-diformylglycocholate (42) and methyl  $\alpha$ -bromoacetoglucuronate were stirred in refluxing anhydrous benzene with cadmium carbonate, the glucuronide acetatemethyl ester derivative (45) was obtained in only 6% yield. This unsatisfactory result was ascribable to difficulties in the separation of the desired product. Therefore, glucuronidation at C-3 followed by conjugation with ethyl glycinate or taurine via the p-nitrophenyl ester was carried out. Condensation of 7,12-diformylcholate 3-glucuronide acetate-methyl ester with p-nitrophenol was effected in ethyl acetate-dioxane by the use of N,N'-dicyclohexylcarbodimide to provide the p-nitrophenyl ester (44). The reaction of the activated ester with ethyl glycinate and taurine proceeded easily, yielding the desired conjugates (45, 46). This method, however, was still unsatisfactory owing to difficulties in the purification step.

The remaining synthetic route starting from the activated ester was then undertaken. The Koenigs-Knorr reaction of p-nitrophenyl 7,12-diformylcholate with  $\alpha$ -acetobromosugar occurred readily to give the glucuronide derivative (44) in reasonable yield. Subsequent condensation with ethyl glycinate and taurine provided the glyco- and tauro-conjugates (45, 46), respectively. On brief exposure to methanolic alkali, elimination of the protecting groups in both the sugar and steroid moieties was effected to give the desired glyco- and taurocholate 3-glucuronides (48, 49) in satisfactory yields.

The 3-glucuronides of glyco- and taurochenodeoxycholates (20, 21) were similarly synthesized using chenodeoxycholic acid 7-formate (12) as a starting compound. Among the three synthetic routes described above, the method involving glucuronidation of the p-nitrophenyl ester and subsequent conversion into the glyco- and tauro-conjugates was found to be most favorable. The desired glucuronides of conjugated deoxycholate (38, 39) and lithocholate (10, 11) were prepared by one of two methods, glucuronidation of the p-nitrophenyl ester and conversion of the unconjugated bile acid 3-glucuronide derivative into the activated ester. The 3-glucuronides of glyco- and tauroursodeoxycholate (29, 30) were synthesized by Koenigs-Knorr reaction of the p-nitrophenyl ester and subsequent transformation into the glyco- and tauro-conjugates.

The nuclear magnetic resonance (NMR) spectra of the glucuronides and their acetate-methyl esters were indicative of the formaton of the  $\beta$ -p-glucopyranuronoside structure. The anomeric proton of the sugar moiety appeared at 4.20—4.46 ppm as a doublet (J=7—9 Hz),

Table I. NMR Spectral Data for the 3-Glucuronides of Bile Acids

C         0.64         0.88         0.88         3.60         4.65         4.04         2.04           K         C         0.64         0.88         0.89         3.60         4.65         4.04         6.04         6.09         2.09           W         M         0.71         0.99 <t< th=""><th>4         C         0.61         0.88         0.88         3.60         4.66         4.04         4.66         4.04         4.66         4.04         4.66         4.04         4.66         4.04         4.66         4.09         4.66         4.09         4.66         4.09         4.66         4.09         4.66         4.09         4.66         4.09         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         8.06         8.06           11         D         0.64         0.92         0.92         0.93         3.48         5.04         4.65         4.02         4.02         8.04         8.06           16         C         0.64         0.92         0.93         3.80         5.04         4.64         4.02         4.02         8.04         8.06           18         M         0.68         0.93         0.93         3.80         4.76         4.64         4.02         4.02         8.04         8.04         8.04           18         M         0.68         0.93         0.93         3.80         4.76</th><th>4         C         0.61         0.88         3.60         4.66         4.08         4.08           8         C         0.64         0.89         0.97         3.60         4.65         4.08           9         W         0.69         0.99         0.99         3.60         4.65         4.08           10         W         0.71         0.99         0.99         3.60         4.65         4.02           11         C         0.64         0.82         0.83         3.48         5.04         4.62         4.02           16         C         0.64         0.92         0.93         3.48         5.04         4.62         4.02           18         C         0.64         0.92         0.93         3.50         5.04         4.62         4.02           18         C         0.64         0.92         0.93         3.50         5.04         4.64         4.02           19         M         0.78         0.93         3.50         3.60         4.76         4.03         4.02           20         C         0.64         0.91         0.92         3.50         3.56         4.43         4.03</th><th>Compd. Solv.a)</th><th>CH<sub>3</sub></th><th>CH3</th><th><math>\widetilde{\operatorname{CH}}_{3}^{b}</math></th><th>-фе Н</th><th><del>ф</del>н</th><th>7<i>α-</i> H</th><th>12<i>6</i>-</th><th><math>c_{1}</math>-H</th><th>nose- C,-H</th><th>NCH₂CO− &gt;</th><th>&gt;NCH₂CO- &gt;NCH₂CH₂S-4&gt; -NH-</th><th>-NH-</th><th>0НЭ-</th><th>-COCH3</th></t<>	4         C         0.61         0.88         0.88         3.60         4.66         4.04         4.66         4.04         4.66         4.04         4.66         4.04         4.66         4.04         4.66         4.09         4.66         4.09         4.66         4.09         4.66         4.09         4.66         4.09         4.66         4.09         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         6.00         8.06         8.06           11         D         0.64         0.92         0.92         0.93         3.48         5.04         4.65         4.02         4.02         8.04         8.06           16         C         0.64         0.92         0.93         3.80         5.04         4.64         4.02         4.02         8.04         8.06           18         M         0.68         0.93         0.93         3.80         4.76         4.64         4.02         4.02         8.04         8.04         8.04           18         M         0.68         0.93         0.93         3.80         4.76	4         C         0.61         0.88         3.60         4.66         4.08         4.08           8         C         0.64         0.89         0.97         3.60         4.65         4.08           9         W         0.69         0.99         0.99         3.60         4.65         4.08           10         W         0.71         0.99         0.99         3.60         4.65         4.02           11         C         0.64         0.82         0.83         3.48         5.04         4.62         4.02           16         C         0.64         0.92         0.93         3.48         5.04         4.62         4.02           18         C         0.64         0.92         0.93         3.50         5.04         4.62         4.02           18         C         0.64         0.92         0.93         3.50         5.04         4.64         4.02           19         M         0.78         0.93         3.50         3.60         4.76         4.03         4.02           20         C         0.64         0.91         0.92         3.50         3.56         4.43         4.03	Compd. Solv.a)	CH <sub>3</sub>	CH3	$\widetilde{\operatorname{CH}}_{3}^{b}$	-фе Н	<del>ф</del> н	7 <i>α-</i> H	12 <i>6</i> -	$c_{1}$ -H	nose- C,-H	NCH₂CO− >	>NCH₂CO- >NCH₂CH₂S-4> -NH-	-NH-	0НЭ-	-COCH3
March   Care	7         C         0.64         0.89<	8 M 0.69 0.95 0.97 3.00 4.65 4.03 110 W/M/C 0.69 0.95 0.95 0.95 0.95 110 W/M/C 0.69 0.95 0.95 0.95 0.95 0.95 0.95 0.95 0.9	O (	0.61	0.88	0.88	3.60				4.66	4.04					2.04 2.06
8         M         0.69         0.89<	8         M         0.09         0.93         0.93         4.094         0.11         0.94         0.95	8 M 0.69 0.99 0.99 11 0 0.69 0.99 0.99 15 0.99 0.99 16 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.9	ی ر	0.04	0.89	0.97	3.60				4.65	4.03			;		2.02 2.05
10   W/M   C   0.69   0.97   0.97   0.99   0.99     11   W/M   C   0.69   0.97   0.97   0.97   0.97   0.99   0.99     12   C   0.64   0.92   0.99   0.99   0.99   0.99   0.99     13   C   0.64   0.92   0.95   3.48   5.04   4.62   4.02   4.054   5.12   8.04   2.01   2.01     13   W/M   C   0.64   0.92   0.95   3.50   5.02   4.64   4.02   4.054   5.12   8.05   8.04   2.01     14   C   0.64   0.92   0.95   3.50   5.02   4.47   4.054   5.12   3.00   3.65   8.05   2.04     15   C   0.64   0.92   0.95   3.50   4.47   4.05   4.054   5.12   3.00   3.65   3.00   3.65   3.00   3.65   4.47   4.05   4.054   5.12   4.054   5.12   4.054   5.12   4.054   5.12   4.054   5.12   4.054   5.12   4.054   5.12   4.054   5.12   4.054   5.12   4.054   5.12   4.054   5.12   4.054	10    W/M/C   0.09	10 W/M/C 0.69 0.97 0.99 11 D 0.61 0.88 0.88 12 C 0.64 0.92 0.97 3.50 5.02 13 C 0.64 0.92 0.95 3.48 5.04 14 C 0.68 0.91 0.95 3.50 5.02 15 C 0.64 0.92 0.95 3.50 5.02 16 C 0.64 0.92 0.95 3.50 5.02 17 C 0.64 0.92 0.95 3.50 5.04 18 M 0.70 0.92 0.95 3.50 5.04 19 M 0.68 0.91 0.95 3.80 10 M 0.68 0.91 0.95 3.80 11 D 0.61 0.95 0.95 3.50 12 W/M 0.68 0.91 0.95 3.80 13 C 0.67 0.95 0.98 3.54 4.76 4.64 14 C 0.72 0.98 0.98 3.50 15 C 0.67 0.95 0.98 16 C/M 0.77 0.92 0.86 17 M 0.77 0.92 0.86 18 M/W 0.70 0.92 0.87 19 M/W 0.70 0.92 0.88 10 0.85 0.94 0.95 11 0.96 0.98 12 0.97 0.97 0.97 13 0.89 0.88 3.50 14 0.70 0.92 0.88 15 C 0.74 0.91 0.85 3.44 5.05 5.25 4.65 16 C/M 0.77 0.92 0.93 3.50 17 0.90 0.93 0.93 3.80 18 M/W 0.70 0.91 0.85 3.44 5.05 5.25 4.62 18 M 0.72 0.93 0.93 3.83 18 C 0.74 0.91 0.85 3.84 5.05 5.25 4.63 18 M/W 0.77 0.92 0.93 3.80 19 M/W 0.77 0.92 0.93 3.80 10 0.77 0.94 0.95 0.97 0.97 10 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.9	) >	40.0	0.00	0.92	9.00				4.65				9.00		2.06
11         M/M         0.61         0.88         0.88         0.88         0.89         3.81s         3.80s         3.80s <td>  10   W/W/C   0.88   0</td> <td>110 W/W</td> <td>TAT</td> <td>0.00</td> <td>cs - c</td> <td>GS -0</td> <td></td> <td></td> <td></td> <td></td> <td>4.28</td> <td></td> <td></td> <td>3.02  3.64</td> <td></td> <td></td> <td>2.03</td>	10   W/W/C   0.88   0	110 W/W	TAT	0.00	cs - c	GS -0					4.28			3.02  3.64			2.03
11         D         C         0.64         0.97         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98 <td>  11   M   M   C   C   C   C   C   C   C   C</td> <td>11 D 0.64 0.97 0.87  11 D 0.64 0.91 0.97 3.50 5.04 4.62 4.02  11 C 0.64 0.91 0.97 3.50 5.02 4.64 4.02  11 D 0.64 0.91 0.95 3.50 5.02 4.64 4.02  11 D 0.64 0.92 0.95 3.50 5.02 4.64 4.02  12 C 0.64 0.91 0.95 3.50 5.04 4.23  20 M 0.68 0.94 0.95 3.50 5.04 4.41  21 W/M 0.68 0.94 0.95 3.80 4.47  22 C 0.67 0.95 0.98 3.54 4.76 4.63 4.02  23 C 0.67 0.95 0.98 3.54 4.76 4.43  24 C 0.72 0.98 0.98 3.56 4.43  35 C/M 0.77 0.96 0.96 3.60 3.60 5.24 4.64 4.04  36 C/M 0.77 0.92 0.97 3.60 5.23 4.04  37 M/W 0.72 0.98 0.89 3.56 5.24 4.64 4.04  38 M/W 0.72 0.98 0.89 3.50 4.75 6.46  4.00 4.50 4.00 0.92 0.97  44 C 0.73 0.89 0.89 3.50 4.00 4.50 4.00 4.50  45 C/M 0.72 0.99 0.93 3.50 4.00 4.50 4.00 4.50  46 C/M 0.72 0.99 0.93 3.50 4.00 4.50 4.00 4.50  47 M 0.72 0.93 1.01 3.84 5.05 5.25 4.62 4.63  48 M/W 0.72 0.93 1.03 3.84 5.05 5.25 4.62 4.03  49 M/W 0.72 0.93 1.03 3.84 5.05 5.25 4.62 4.03  40 0.72 0.93 1.03 3.84 5.05 5.25 4.62 4.03  41 C 0.74 0.91 0.82 3.44 5.03 5.25 4.62 4.03  42 C 0.74 0.91 0.82 3.44 5.03 5.25 4.62  44 C 0.79 0.93 1.03 3.84 4.00 4.47  45 C/M 0.82 0.93 1.03 3.84 4.00 4.47  46 C/M 0.82 0.93 1.03 3.84 4.00 4.47  47 M 0.72 0.93 1.04 3.84 4.00 4.47  48 M/W 0.77 0.92 0.99 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 3.64 1.00  40 0.70 0.90 0.90 0.90 0.90 3.00  41 0.72 0.93 1.03 3.84 4.00 4.47  42 C 0.74 0.91 0.82 0.90 3.64 1.00  43 0.75 0.90 0.90 0.90 0.90 3.00  44 0.75 0.90 0.90 0.90 0.90 0.90 3.00  45 0.74 0.91 0.82 0.97 0.89  46 0.74 0.91 0.82 0.97 0.89  47 M 0.72 0.93 1.04 3.84 4.00 4.47  48 M/W 0.72 0.90 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 0.90 0.90 0.90 0.90 0.90 0.90</td> <td>M E</td> <td>0.71</td> <td>0.99</td> <td>0.99</td> <td></td>	11   M   M   C   C   C   C   C   C   C   C	11 D 0.64 0.97 0.87  11 D 0.64 0.91 0.97 3.50 5.04 4.62 4.02  11 C 0.64 0.91 0.97 3.50 5.02 4.64 4.02  11 D 0.64 0.91 0.95 3.50 5.02 4.64 4.02  11 D 0.64 0.92 0.95 3.50 5.02 4.64 4.02  12 C 0.64 0.91 0.95 3.50 5.04 4.23  20 M 0.68 0.94 0.95 3.50 5.04 4.41  21 W/M 0.68 0.94 0.95 3.80 4.47  22 C 0.67 0.95 0.98 3.54 4.76 4.63 4.02  23 C 0.67 0.95 0.98 3.54 4.76 4.43  24 C 0.72 0.98 0.98 3.56 4.43  35 C/M 0.77 0.96 0.96 3.60 3.60 5.24 4.64 4.04  36 C/M 0.77 0.92 0.97 3.60 5.23 4.04  37 M/W 0.72 0.98 0.89 3.56 5.24 4.64 4.04  38 M/W 0.72 0.98 0.89 3.50 4.75 6.46  4.00 4.50 4.00 0.92 0.97  44 C 0.73 0.89 0.89 3.50 4.00 4.50 4.00 4.50  45 C/M 0.72 0.99 0.93 3.50 4.00 4.50 4.00 4.50  46 C/M 0.72 0.99 0.93 3.50 4.00 4.50 4.00 4.50  47 M 0.72 0.93 1.01 3.84 5.05 5.25 4.62 4.63  48 M/W 0.72 0.93 1.03 3.84 5.05 5.25 4.62 4.03  49 M/W 0.72 0.93 1.03 3.84 5.05 5.25 4.62 4.03  40 0.72 0.93 1.03 3.84 5.05 5.25 4.62 4.03  41 C 0.74 0.91 0.82 3.44 5.03 5.25 4.62 4.03  42 C 0.74 0.91 0.82 3.44 5.03 5.25 4.62  44 C 0.79 0.93 1.03 3.84 4.00 4.47  45 C/M 0.82 0.93 1.03 3.84 4.00 4.47  46 C/M 0.82 0.93 1.03 3.84 4.00 4.47  47 M 0.72 0.93 1.04 3.84 4.00 4.47  48 M/W 0.77 0.92 0.99 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 3.64 1.00  40 0.70 0.90 0.90 0.90 0.90 3.00  41 0.72 0.93 1.03 3.84 4.00 4.47  42 C 0.74 0.91 0.82 0.90 3.64 1.00  43 0.75 0.90 0.90 0.90 0.90 3.00  44 0.75 0.90 0.90 0.90 0.90 0.90 3.00  45 0.74 0.91 0.82 0.97 0.89  46 0.74 0.91 0.82 0.97 0.89  47 M 0.72 0.93 1.04 3.84 4.00 4.47  48 M/W 0.72 0.90 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 0.90 0.90 0.90 0.90 0.90 0.90	M E	0.71	0.99	0.99											
11   D   0.61   0.88   0.88   0.88   0.88   0.88   0.89   0.89   0.92   0.92   0.92   0.92   0.92   0.92   0.92   0.92   0.93   0.92   0.93	15   C   0.64   0.28   0.88   0.88   0.88   0.88   0.88   0.88   0.88   0.88   0.88   0.88   0.88   0.88   0.88   0.88   0.89   0.89   0.80   0.90   0.97   0.90   0.97   0.90	11 D 0.61 0.88 0.88 4.29 11 C 0.64 0.92 0.92 3.48 5.04 4.62 4.02 11 C 0.64 0.92 0.92 3.48 5.04 4.64 4.64 118 M 0.70 0.97 0.97 3.50 5.04 4.64 119 M 0.68 0.91 0.97 3.50 5.04 4.64 120 M 0.68 0.91 0.95 3.80 4.41 121 W/M 0.68 0.91 0.95 3.54 4.76 4.64 4.02 122 W/M 0.68 0.94 0.95 3.54 4.76 4.64 4.02 123 W/M 0.68 0.94 0.95 3.54 4.76 4.64 4.02 124 C 0.67 0.95 0.98 3.54 4.76 4.64 4.02 125 C 0.69 0.95 0.98 3.54 4.76 4.64 4.04 126 C 0.67 0.96 0.98 3.54 4.76 4.43 127 M 0.72 0.98 0.98 3.56 4.43 128 M/W 0.70 0.92 0.97 3.60 5.23 4.20 139 M/W 0.70 0.92 0.97 3.60 5.22 4.60 4.00 140 0.72 0.93 1.01 3.50 4.00 4.50 141 C 0.74 0.91 0.82 3.44 5.03 5.25 4.62 142 C 0.74 0.91 0.82 3.44 5.03 5.25 4.63 143 C 0.74 0.91 0.82 3.44 5.03 5.25 4.63 144 C 0.77 0.92 0.97 0.89 3.84 4.43 145 C 0.74 0.91 0.82 3.44 5.03 5.25 4.62 146 C/M 0.82 0.93 1.03 3.84 4.00 4.47 148 M 0.72 0.93 1.03 3.84 4.00 4.47 149 M/W 0.71 0.92 0.97 0.89 3.84 4.00 4.47 140 0.72 0.93 1.03 3.84 4.00 4.47 150 0.72 0.93 1.03 3.84 4.00 4.47 150 0.72 0.93 1.03 3.84 4.00 4.47 150 0.72 0.94 0.91 0.85 3.84 4.00 4.47 150 0.74 0.91 0.82 0.97 0.89 5.06 5.26 5.26 5.26 5.26 5.26 5.26 5.26 5.2	W/M/C	0.69	0.97	0.97							3.81s				
15   C   0.64   0.92   0.92   3.48   5.04   4.02   4.64   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02   4.04   4.02	16   C   0.64   0.92   0.92   3.48   5.04   4.64   4.02   4.02   4.03	115 C 0.64 0.92 0.92 3.48 5.04 4.62 4.02 1.16 C 0.64 0.92 0.92 3.48 5.04 4.62 1.64 4.02 1.8 1.8 1.8 M 0.68 0.91 0.95 3.50 5.04 4.41 4.02 2.0 M 0.68 0.91 0.95 3.50 5.04 4.41 4.02 2.0 M 0.68 0.92 0.97 3.80 4.42 4.47 4.62 2.0 0.67 0.95 0.93 3.54 4.76 4.63 4.02 2.0 0.67 0.95 0.98 3.54 4.76 4.63 4.02 2.0 0.67 0.95 0.98 3.54 4.76 4.63 4.02 2.0 0.07 0.96 0.98 3.50 4.76 4.63 4.02 2.0 M 0.72 0.98 0.98 3.50 4.76 4.64 4.04 3.0 0.72 0.98 0.98 3.56 3.56 4.43 3.56 4.43 3.56 4.44 3.56 0.09 0.98 3.56 4.00 4.00 0.00 0.00 0.00 0.00 0.00 0.0	Д	0.61	0.88	0.88					4.29						
16         C         0.64         0.91         0.97         3.50         5.02         4.64         4.02         4.054         5.95         8.04         2.01           18         C         0.64         0.92         0.93         3.50         5.04         4.93         4.64         4.054         5.95         8.04         2.01           19         M         0.68         0.91         0.95         3.80         4.41         3.76         3.00         3.65         8.04         2.02           21         M         0.68         0.91         0.95         3.80         4.42         3.76         3.00         3.65         8.04         2.02           24         C         0.67         0.95         0.91         3.50         4.76         4.64         4.02         3.00         3.65         1.96         3.00         3.60         1.96         4.63         4.024         3.75         3.00         3.69         1.96         3.77s         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024         4.024	17   C   0.64   0.91   0.97   3.55   5.02   4.64   4.02   4.64   4.02   4.64   4.02   4.64   4.02   4.64   4.02   4.64   4.02   4.64   4.02   4.02   4.02	16 C 0.64 0.91 0.97 3.50 5.02 4.64 4.02  17 C 0.64 0.92 0.95 3.50 5.04 4.64  20 M 0.68 0.92 0.97 3.80 4.41  21 W/M 0.68 0.92 0.97 3.80 4.47  22 C 0.67 0.95 0.91 3.50 4.76 4.64  23 C 0.67 0.95 0.91 3.50 4.76 4.64  24 C 0.67 0.95 0.98 3.54 4.76 4.63  25 C 0.69 0.95 0.98 3.54 4.76 4.64  26 C 0.67 0.97 0.97 3.80 4.42  27 M 0.72 0.98 0.98 3.56 4.44  28 M/W 0.70 0.96 0.98 3.56 4.64  30 M/W 0.70 0.96 0.98 3.56 4.64  31 C 0.72 0.88 0.89 3.56 4.67  32 C 0.73 0.89 0.83 3.60 5.23 4.00 4.50  34 C 0.75 0.99 0.95 3.44 5.03 5.23 4.60  44 C 0.79 0.92 0.97 3.44 5.03 5.25 4.65  44 C 0.74 0.91 0.85 3.44 5.03 5.25 4.65  45 C M/W 0.72 0.99 0.99 3.89 3.50  46 C/M 0.72 0.99 0.99 3.89 3.80  47 M 0.72 0.90 0.90 3.89 3.80  48 M 0.72 0.91 0.85 3.44 5.05 5.25 4.62  47 M 0.72 0.92 0.99 3.89  48 M 0.72 0.99 0.99 3.89  49 M/W 0.71 0.92 0.99 3.89  40 M/W 0.77 0.92 0.99 3.89  41 0.72 0.99 0.90 3.89  42 C 0.74 0.91 0.85 3.44 5.05 5.25 4.62  44 0.74 0.91 0.85 3.44 5.05 5.25 4.62  45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.62  46 C/M 0.82 0.97 0.89 3.89  47 M 0.77 0.92 0.99 3.89  48 M 0.72 0.99 1.04  49 M/W 0.71 0.99 0.99 3.89  40 0.71 0.99 0.99 3.89  41 0.72 0.99 1.04  42 0.74 0.91 0.85 3.44 5.05 5.25 4.65  44 0.75 0.99 0.99 3.89  45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.65  46 C/M 0.82 0.97 0.89 3.89  47 M 0.77 0.90 0.90 0.90 3.89  48 M 0.72 0.99 1.04  49 M/W 0.71 0.95 0.99 3.89  40 0.71 0.90 0.90 0.90 3.89  41 0.72 0.99 1.04  42 0.74 0.91 0.85 3.44 5.05 5.25 4.65  44 0.74 0.91 0.85 3.44 5.05  45 0.75 0.90 0.90 0.90 3.89  47 0.77 0.90 0.90 0.90 0.90 3.89  48 M 0.72 0.90 0.90 0.90 0.90  40 0.71 0.90 0.90 0.90 0.90  41 0.71 0.90 0.90 0.90 0.90  42 0.72 0.90 0.90 0.90 0.90  43 0.74 0.91 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90 0.90  44 0.75 0.90 0.90 0.90 0.90  44 0.75	Ö	0.64	0.92	0.92	3.48	5.04			4.62	4.02				8 06	
I/I         C         0.64         0.92         0.93         5.04         4.64         4.054         5Hz         5.95         8.02         2.04           19         M         0.78         0.97         0.97         3.80         4.42         4.30         4.054         5.04         4.83         5.04         4.83         5.04         4.83         5.04         4.83         5.04         4.83         5.04         4.83         5.04         4.83         3.80         3.80         3.80         2.02         3.80         4.42         3.76         3.00         3.56         3.83         4.74         4.76         4.64         4.02         3.00         3.56         3.90         3.50         1.96         1.96         2.02         3.80         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         4.44         4.02         4.04         4.02         3.00         3.56         4.44         4.02         4.02         3.00         3.06         4.44         4.02         4.04         4.02         4.04         4.02         4.04         4.02         4.02         4.02         4.02         4.02         4.02         4.02         4.02         4.02	17     C	17       C       0.64       0.92       0.95       3.50       5.04       4.64         18       M       0.70       0.97       0.97       3.50       5.04       4.30         20       M       0.68       0.91       0.95       3.80       4.41         21       W/M       0.68       0.94       0.95       3.80       4.76       4.64       4.02         25       C       0.67       0.95       0.91       3.50       4.76       4.64       4.02         26       C       0.69       0.95       0.98       3.54       4.76       4.64       4.02         26       C       0.69       0.95       0.98       3.54       4.76       4.64       4.02         27       M       0.72       0.98       0.98       3.50       4.76       4.64       4.04         28       M       0.71       0.96       0.98       3.56       4.76       4.64       4.04         29       M       0.71       0.96       0.98       3.56       4.76       4.64       4.04         39       M/W       0.70       0.99       0.98       3.56       4.76       4.64	ပ	0.64	0.91	0.97	3.50	5.05			4.64	4.02				8.04	2.01.2.04
18         M         0.70         0.97         0.97         5.04         4.30         4.30         3.02 3.65         8.18         2.02           20         M         0.68         0.92         0.95         3.80         4.47         3.76         3.00 3.56         8.18         2.02           21         W/M         0.68         0.94         0.95         3.80         4.76         4.47         4.64         4.02         3.00 3.56         1.97           25         C         0.69         0.95         0.98         3.54         4.76         4.64         4.02         4.024         5.95         1.96         1.97           26         C         0.67         0.95         0.98         3.50         4.76         4.64         4.02         4.024         5.95         1.197         1.196         1.197           27         O         0.66         0.98         3.50         4.76         4.64         4.04         3.775         3.08 3.61         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96	18         M         0.70         0.97         0.97         5.04         4.30         3.02 3.65         8.18         2.02 2.03 2.07           20         M         0.68         0.91         0.97         3.80         4.41         3.76         3.00 3.56         8.18         2.02 2.03         2.07           21         WA         0.68         0.92         0.97         3.80         4.41         3.76         3.00 3.56         1.97 2.03 2.03         2.02         2.03         3.00         3.50         3.75         3.00 3.56 </td <td>18 M 0.70 0.97 0.97 5.04 4.30  20 M 0.68 0.91 0.95 3.80 4.41  21 W/M 0.68 0.92 0.97 3.80 4.42  22 C 0.69 0.95 0.98 3.54 4.76 4.63 4.02  23 C 0.67 0.95 0.98 3.50 4.76 4.63  24 M 0.72 0.98 0.98 3.50 4.76 4.63  25 M 0.72 0.98 0.98 3.50 4.76 4.63  26 C 0.67 0.95 0.98 3.50 4.76 4.63  27 M 0.72 0.98 0.98 3.50 4.76 4.63  38 M/W 0.70 0.96 0.96 3.60 3.60 3.60  39 C 0.72 0.89 0.89 3.56 5.24 4.64 4.04  31 C 0.73 0.89 0.89 3.56 5.23 4.20  32 M/W 0.77 0.92 0.86 3.60 5.23 4.00  43 C 0.74 0.91 0.82 3.44 5.03 5.25 4.65  44 C 0.74 0.91 0.82 3.44 5.03 5.26 4.65  45 C 0.74 0.91 0.82 3.44 5.03 5.26 4.65  46 C/M 0.72 0.93 1.03 3.83  47 M 0.72 0.93 1.03 3.83  48 M 0.72 0.93 1.03 3.84 5.05 5.25 4.60  49 M/W 0.70 0.92 0.99 3.88  40 0.70 0.92 0.99 3.88  41 C 0.74 0.91 0.82 3.44 5.05 5.25 4.60  42 C 0.74 0.91 0.85 3.84 5.05 5.25 4.60  43 M/W 0.77 0.92 0.99 3.88  44 C 0.79 0.92 0.99 3.88  45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  46 C/M 0.82 0.97 0.89 5.06  47 M 0.72 0.93 1.03 3.84 5.05  48 M 0.72 0.93 1.03 3.84  49 M/W 0.71 0.92 0.99 3.88  40 M/W 0.71 0.92 0.99 3.88  41 C 0.74 0.91 0.85 3.84  42 M/W 0.71 0.92 0.99 3.88  43 M/W 0.71 0.92 0.99 3.88  44 C 0.74 0.91 0.85 3.84  45 C 0.74 0.91 0.85 3.84  47 M 0.75 0.99 1.08  48 M 0.77 0.90 0.90  49 doublet, J=-0.19.π.  40 doublet, J=-0.19.π.  50 doublet, J=-0.19.π.  50 doublet, J=-0.19.π.  50 doublet, J=-0.19.π.  50 doublet, J=-0.19.π.</td> <td>ပ</td> <td>0.64</td> <td>0.92</td> <td>0.95</td> <td>3.50</td> <td>5.04</td> <td></td> <td></td> <td>4.64</td> <td></td> <td></td> <td></td> <td>5 95</td> <td>8.02</td> <td>2.01</td>	18 M 0.70 0.97 0.97 5.04 4.30  20 M 0.68 0.91 0.95 3.80 4.41  21 W/M 0.68 0.92 0.97 3.80 4.42  22 C 0.69 0.95 0.98 3.54 4.76 4.63 4.02  23 C 0.67 0.95 0.98 3.50 4.76 4.63  24 M 0.72 0.98 0.98 3.50 4.76 4.63  25 M 0.72 0.98 0.98 3.50 4.76 4.63  26 C 0.67 0.95 0.98 3.50 4.76 4.63  27 M 0.72 0.98 0.98 3.50 4.76 4.63  38 M/W 0.70 0.96 0.96 3.60 3.60 3.60  39 C 0.72 0.89 0.89 3.56 5.24 4.64 4.04  31 C 0.73 0.89 0.89 3.56 5.23 4.20  32 M/W 0.77 0.92 0.86 3.60 5.23 4.00  43 C 0.74 0.91 0.82 3.44 5.03 5.25 4.65  44 C 0.74 0.91 0.82 3.44 5.03 5.26 4.65  45 C 0.74 0.91 0.82 3.44 5.03 5.26 4.65  46 C/M 0.72 0.93 1.03 3.83  47 M 0.72 0.93 1.03 3.83  48 M 0.72 0.93 1.03 3.84 5.05 5.25 4.60  49 M/W 0.70 0.92 0.99 3.88  40 0.70 0.92 0.99 3.88  41 C 0.74 0.91 0.82 3.44 5.05 5.25 4.60  42 C 0.74 0.91 0.85 3.84 5.05 5.25 4.60  43 M/W 0.77 0.92 0.99 3.88  44 C 0.79 0.92 0.99 3.88  45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  46 C/M 0.82 0.97 0.89 5.06  47 M 0.72 0.93 1.03 3.84 5.05  48 M 0.72 0.93 1.03 3.84  49 M/W 0.71 0.92 0.99 3.88  40 M/W 0.71 0.92 0.99 3.88  41 C 0.74 0.91 0.85 3.84  42 M/W 0.71 0.92 0.99 3.88  43 M/W 0.71 0.92 0.99 3.88  44 C 0.74 0.91 0.85 3.84  45 C 0.74 0.91 0.85 3.84  47 M 0.75 0.99 1.08  48 M 0.77 0.90 0.90  49 doublet, J=-0.19.π.  40 doublet, J=-0.19.π.  50 doublet, J=-0.19.π.  50 doublet, J=-0.19.π.  50 doublet, J=-0.19.π.  50 doublet, J=-0.19.π.	ပ	0.64	0.92	0.95	3.50	5.04			4.64				5 95	8.02	2.01
19         M         0.68         0.91         0.95         3.89         4.41         3.76         3.00         3.56         4.47         3.00         3.56         1.97         1.97           24         C         0.67         0.95         0.91         3.80         4.76         4.64         4.02         3.00         3.56         1.96         1.97           25         C         0.68         0.95         0.93         3.54         4.76         4.64         4.02         4.02         1.96         1.96           25         C         0.68         0.95         0.93         3.56         4.76         4.63         4.02         4.02         1.96         1.96           26         C         0.67         0.95         0.93         3.56         4.76         4.63         4.02         1.96         1.96           27         O         0.77         0.95         0.93         3.56         4.44         3.77s         3.03         3.63         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.96         1.97         1.96         1.96         1.96         1.96         1.96 <th< td=""><td>19         M         0.68         0.99         0.95         3.80         4.41         3.76         3.00         3.56         1.97         2.03         2.03         2.03         2.03         2.03         2.03         2.03         2.03         3.80         4.47         4.42         3.76         3.00         3.56         1.97         2.03         2.03         2.03         2.03         3.00         3.63         4.47         4.44         3.75         4.02d, 5Hz         2.98         3.61         1.99         2.03         2.03         2.03         2.03         3.00         3.56         4.44         3.77s         3.03         3.61         1.96         1.98         1.99         &lt;</td><td>19 M 0.68 0.91 0.95 3.80 4.41  20 M 0.68 0.92 0.97 3.80 4.76  21 W/M 0.68 0.92 0.97 3.80 4.76  22 C 0.69 0.99 0.98 3.54 4.76 4.63  23 C 0.67 0.96 0.98 3.50 4.76 4.63  24 C 0.67 0.98 0.98 3.54 4.76 4.63  25 M 0.72 0.98 0.98 3.50 4.76 4.63  26 C 0.67 0.98 0.98 3.50 4.76 4.63  27 M 0.72 0.98 0.88 3.60 4.76 4.44  28 C 0.75 0.89 0.89 3.56 5.24 4.64 4.04  29 M/W 0.70 0.96 0.98 3.50 5.24 4.64 4.04  29 M/W 0.71 0.92 0.86 3.60 5.23 4.20  31 C 0.72 0.98 0.83 3.60 5.23 4.20  32 C 0.73 0.89 0.83 3.60 5.23 4.20  34 C 0.77 0.92 0.86 3.60 5.23 4.00  44 C 0.77 0.92 0.86 3.60 5.23 4.20  45 C 0.77 0.92 0.86 3.60 5.23 4.00  46 C/M 0.77 0.92 0.86 3.60 5.26 4.65  47 M 0.72 0.93 1.01 8.2 3.44 5.03 5.25 4.60  48 M/W 0.70 0.92 0.93 3.50 5.20 4.00  49 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  40 0.77 0.92 0.93 3.80  41 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  42 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  43 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  44 C 0.79 0.92 0.93 3.50  45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  46 C/M 0.72 0.93 1.03 3.88 4.43  47 M 0.72 0.92 1.04 3.84 5.00 4.00 4.47  48 M 0.72 0.92 1.04 3.84 5.00 4.00 4.47  49 M/W 0.71 0.92 0.99 3.84 5.00  40 d.thplet, J=6-7Hz.  50 doublet, J=10.14.  50 doublet, J=10.14.</td><td>M</td><td>0.70</td><td>0.97</td><td>0.97</td><td></td><td>5.04</td><td></td><td></td><td>4.30</td><td></td><td></td><td>3.02 3.65</td><td></td><td>20.00</td><td>2 03</td></th<>	19         M         0.68         0.99         0.95         3.80         4.41         3.76         3.00         3.56         1.97         2.03         2.03         2.03         2.03         2.03         2.03         2.03         2.03         3.80         4.47         4.42         3.76         3.00         3.56         1.97         2.03         2.03         2.03         2.03         3.00         3.63         4.47         4.44         3.75         4.02d, 5Hz         2.98         3.61         1.99         2.03         2.03         2.03         2.03         3.00         3.56         4.44         3.77s         3.03         3.61         1.96         1.98         1.99         <	19 M 0.68 0.91 0.95 3.80 4.41  20 M 0.68 0.92 0.97 3.80 4.76  21 W/M 0.68 0.92 0.97 3.80 4.76  22 C 0.69 0.99 0.98 3.54 4.76 4.63  23 C 0.67 0.96 0.98 3.50 4.76 4.63  24 C 0.67 0.98 0.98 3.54 4.76 4.63  25 M 0.72 0.98 0.98 3.50 4.76 4.63  26 C 0.67 0.98 0.98 3.50 4.76 4.63  27 M 0.72 0.98 0.88 3.60 4.76 4.44  28 C 0.75 0.89 0.89 3.56 5.24 4.64 4.04  29 M/W 0.70 0.96 0.98 3.50 5.24 4.64 4.04  29 M/W 0.71 0.92 0.86 3.60 5.23 4.20  31 C 0.72 0.98 0.83 3.60 5.23 4.20  32 C 0.73 0.89 0.83 3.60 5.23 4.20  34 C 0.77 0.92 0.86 3.60 5.23 4.00  44 C 0.77 0.92 0.86 3.60 5.23 4.20  45 C 0.77 0.92 0.86 3.60 5.23 4.00  46 C/M 0.77 0.92 0.86 3.60 5.26 4.65  47 M 0.72 0.93 1.01 8.2 3.44 5.03 5.25 4.60  48 M/W 0.70 0.92 0.93 3.50 5.20 4.00  49 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  40 0.77 0.92 0.93 3.80  41 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  42 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  43 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  44 C 0.79 0.92 0.93 3.50  45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.60  46 C/M 0.72 0.93 1.03 3.88 4.43  47 M 0.72 0.92 1.04 3.84 5.00 4.00 4.47  48 M 0.72 0.92 1.04 3.84 5.00 4.00 4.47  49 M/W 0.71 0.92 0.99 3.84 5.00  40 d.thplet, J=6-7Hz.  50 doublet, J=10.14.	M	0.70	0.97	0.97		5.04			4.30			3.02 3.65		20.00	2 03
20         M         0.68         0.92         0.97         3.80         4.42         3.76         3.76         3.00         3.56         4.42         3.76         3.00         3.56         4.02         4.44         4.02	21         M         0.68         0.94         0.95         3.80         4.44         7.6         4.47         3.00         3.56         1.97         2.08         2.05         2.09         2.09         2.09         2.09         2.09         2.09         2.09         3.80         4.44         4.64         4.64         4.64         4.64         4.64         4.64         4.65         4.02         3.00         3.56         1.97         2.08         2.09         2.09         2.09         2.09         2.09         2.09         3.56         4.64         4.02         4.02         3.00         3.56         1.96         2.09         1.96         2.09         1.96         2.09         2.09         2.09         3.56         4.63         4.02         4.02         3.00         3.56         1.96         2.09         1.99         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09         1.96         2.09<	20 M 0.68 0.92 0.97 3.80 4.42  21 W/M 0.68 0.94 0.95 3.82 4.76 4.64 4.02  25 C 0.67 0.95 0.98 3.54 4.76 4.63 4.02  26 C 0.67 0.95 0.98 3.50 4.76 4.63  27 M 0.72 0.98 0.98 3.50 4.76 4.63  28 M 0.74 0.97 0.97 8.80 3.50 4.44  30 M/W 0.70 0.96 0.98 3.56 5.24 4.64 4.04  31 C 0.72 0.88 0.80 3.60 5.23 4.20  32 C 0.73 0.89 0.83 3.60 5.23 4.20  33 C 0.73 0.89 0.83 3.60 5.23 4.00  44 C 0.77 0.93 1.01 3.98 4.45  45 C 0.74 0.91 0.85 3.44 5.03 5.25 4.65  47 M 0.72 0.92 0.97 3.84 5.03 5.25 4.65  48 M 0.72 0.92 1.04 3.84 4.00 4.47  49 M/W 0.72 0.92 1.03 3.84 5.05 5.25 4.60  41 M 0.72 0.92 1.03 3.84 5.05 5.25 4.65  42 M/W 0.72 0.92 1.03 3.84 4.00 4.47  43 C 0.74 0.91 0.85 3.44 5.03 5.25 4.60  44 C 0.74 0.91 0.85 3.44 5.03 5.25 4.60  45 C M 0.72 0.92 1.03 3.84 4.00 4.47  46 C M 0.72 0.92 1.03 3.84 4.00 4.47  47 M 0.72 0.92 1.03 3.84 4.00 4.47  48 M 0.72 0.92 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 3.84 5.05 5.25 5.25 4.60  44 M 0.72 0.92 1.04 3.84 4.00 4.47  45 C 0.74 0.91 0.85 3.44 5.05 5.25 5.25 4.60  46 M/W 0.72 0.92 1.04 3.84 4.00 4.47  47 M 0.72 0.92 1.04 3.84 4.00 4.47  48 M 0.72 0.92 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 3.84 4.43  49 M/W 0.71 0.92 0.99 3.84 4.43  40 M/W 0.72 0.96 1.00  41 M/W 0.72 0.96 1.00  42 M/W 0.74 0.91 0.85 3.44 5.05 5.25 5.25 5.25 5.25 5.25 5.25 5.25	M	0.68	0.91	0.92		3.80			4.41						3
21         W/M         0.68         0.94         0.95         3.82         4.47         3.00         3.56           25         C         0.67         0.95         0.98         3.54         4.76         4.64         4.02         3.00         3.56         4.76         4.64         4.02         3.00         3.56         4.76         4.64         4.02         4.024         5.95         3.00         3.56         4.76         4.64         4.02         4.024         5.95         3.00         3.56         1.96 <td>21         W/M         0.68         0.94         0.95         3.82         4.47         3.00         3.56         1.97         2.08         2.09         2.00         2.00         3.56         4.47         4.64         4.02         4.024         5.18         5.95         1.97         2.08         2.09         2.00         2.00         2.99         3.50         4.76         4.63         4.024         5.18         2.98         3.61         1.96         2.09         1.96         2.00         2.00         3.00         3.50         4.76         4.63         4.024         5.18         2.98         3.61         1.96         2.09         1.96         2.09         1.99         2.00         2.00         1.90         2.00         1.90         2.00         2.00         1.90         2.00         2.00         1.90         1.90         2.00         1.90         <t< td=""><td>21 W/M 0.68 0.94 · 0.95 3.82 4.47  24 C 0.67 0.95 0.91 3.50 4.76 4.63 4.02  25 C 0.69 0.95 0.98 3.54 4.76 4.63 4.02  28 M 0.72 0.98 0.98 3.50 4.76 4.63 4.02  29 M 0.71 0.96 0.98 3.50 4.76 4.43  30 M/W 0.70 0.96 0.98 3.56 4.43  31 C 0.72 0.88 0.80 3.60 3.56 4.43  32 C 0.72 0.88 0.80 3.56 5.24 4.64 4.04  33 C 0.72 0.98 0.83 3.60 5.23 4.20  34 C 0.75 0.89 0.83 3.60 5.23 4.20  35 C 0.77 0.92 0.86 1.00 5.23 4.00 4.07  36 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00  44 C 0.74 0.91 0.85 3.44 5.03 5.22 4.60  45 C 0.74 0.91 0.85 3.44 5.03 5.22 4.60  46 C/M 0.82 0.97 0.93 3.89 5.06 5.26 4.22  47 C 0.74 0.91 0.85 3.44 5.03 5.25 4.62  48 M 0.72 0.93 1.03 3.84 4.00 4.47  49 M/W 0.71 0.92 0.94 3.84 5.05 5.25 4.65  40 0.71 0.92 0.91 0.85 3.44 5.05 5.25 2.6 5.25  41 M 0.72 0.92 1.04 3.84 4.00 4.47  42 C 0.74 0.91 0.85 3.44 5.05 5.25 4.65  44 M 0.72 0.92 1.04 3.84 4.00 4.47  45 M 0.72 0.92 1.04 3.84 4.00 4.47  47 C 0.74 0.91 0.85 3.44 5.05 5.05 5.25 2.6  48 M 0.72 0.92 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 3.89  40 D.71 0.92 0.99 3.89  41 D.72 0.92 1.04 3.84  42 D.73 0.90 1.00 1.00 1.00 1.00 1.00 1.00 1.00</td><td>M</td><td>0.68</td><td>0.92</td><td>0.97</td><td></td><td>3.80</td><td></td><td></td><td>4.42</td><td></td><td>3.76</td><td></td><td></td><td></td><td></td></t<></td>	21         W/M         0.68         0.94         0.95         3.82         4.47         3.00         3.56         1.97         2.08         2.09         2.00         2.00         3.56         4.47         4.64         4.02         4.024         5.18         5.95         1.97         2.08         2.09         2.00         2.00         2.99         3.50         4.76         4.63         4.024         5.18         2.98         3.61         1.96         2.09         1.96         2.00         2.00         3.00         3.50         4.76         4.63         4.024         5.18         2.98         3.61         1.96         2.09         1.96         2.09         1.99         2.00         2.00         1.90         2.00         1.90         2.00         2.00         1.90         2.00         2.00         1.90         1.90         2.00         1.90 <t< td=""><td>21 W/M 0.68 0.94 · 0.95 3.82 4.47  24 C 0.67 0.95 0.91 3.50 4.76 4.63 4.02  25 C 0.69 0.95 0.98 3.54 4.76 4.63 4.02  28 M 0.72 0.98 0.98 3.50 4.76 4.63 4.02  29 M 0.71 0.96 0.98 3.50 4.76 4.43  30 M/W 0.70 0.96 0.98 3.56 4.43  31 C 0.72 0.88 0.80 3.60 3.56 4.43  32 C 0.72 0.88 0.80 3.56 5.24 4.64 4.04  33 C 0.72 0.98 0.83 3.60 5.23 4.20  34 C 0.75 0.89 0.83 3.60 5.23 4.20  35 C 0.77 0.92 0.86 1.00 5.23 4.00 4.07  36 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00  44 C 0.74 0.91 0.85 3.44 5.03 5.22 4.60  45 C 0.74 0.91 0.85 3.44 5.03 5.22 4.60  46 C/M 0.82 0.97 0.93 3.89 5.06 5.26 4.22  47 C 0.74 0.91 0.85 3.44 5.03 5.25 4.62  48 M 0.72 0.93 1.03 3.84 4.00 4.47  49 M/W 0.71 0.92 0.94 3.84 5.05 5.25 4.65  40 0.71 0.92 0.91 0.85 3.44 5.05 5.25 2.6 5.25  41 M 0.72 0.92 1.04 3.84 4.00 4.47  42 C 0.74 0.91 0.85 3.44 5.05 5.25 4.65  44 M 0.72 0.92 1.04 3.84 4.00 4.47  45 M 0.72 0.92 1.04 3.84 4.00 4.47  47 C 0.74 0.91 0.85 3.44 5.05 5.05 5.25 2.6  48 M 0.72 0.92 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 3.89  40 D.71 0.92 0.99 3.89  41 D.72 0.92 1.04 3.84  42 D.73 0.90 1.00 1.00 1.00 1.00 1.00 1.00 1.00</td><td>M</td><td>0.68</td><td>0.92</td><td>0.97</td><td></td><td>3.80</td><td></td><td></td><td>4.42</td><td></td><td>3.76</td><td></td><td></td><td></td><td></td></t<>	21 W/M 0.68 0.94 · 0.95 3.82 4.47  24 C 0.67 0.95 0.91 3.50 4.76 4.63 4.02  25 C 0.69 0.95 0.98 3.54 4.76 4.63 4.02  28 M 0.72 0.98 0.98 3.50 4.76 4.63 4.02  29 M 0.71 0.96 0.98 3.50 4.76 4.43  30 M/W 0.70 0.96 0.98 3.56 4.43  31 C 0.72 0.88 0.80 3.60 3.56 4.43  32 C 0.72 0.88 0.80 3.56 5.24 4.64 4.04  33 C 0.72 0.98 0.83 3.60 5.23 4.20  34 C 0.75 0.89 0.83 3.60 5.23 4.20  35 C 0.77 0.92 0.86 1.00 5.23 4.00 4.07  36 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00  44 C 0.74 0.91 0.85 3.44 5.03 5.22 4.60  45 C 0.74 0.91 0.85 3.44 5.03 5.22 4.60  46 C/M 0.82 0.97 0.93 3.89 5.06 5.26 4.22  47 C 0.74 0.91 0.85 3.44 5.03 5.25 4.62  48 M 0.72 0.93 1.03 3.84 4.00 4.47  49 M/W 0.71 0.92 0.94 3.84 5.05 5.25 4.65  40 0.71 0.92 0.91 0.85 3.44 5.05 5.25 2.6 5.25  41 M 0.72 0.92 1.04 3.84 4.00 4.47  42 C 0.74 0.91 0.85 3.44 5.05 5.25 4.65  44 M 0.72 0.92 1.04 3.84 4.00 4.47  45 M 0.72 0.92 1.04 3.84 4.00 4.47  47 C 0.74 0.91 0.85 3.44 5.05 5.05 5.25 2.6  48 M 0.72 0.92 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 3.89  40 D.71 0.92 0.99 3.89  41 D.72 0.92 1.04 3.84  42 D.73 0.90 1.00 1.00 1.00 1.00 1.00 1.00 1.00	M	0.68	0.92	0.97		3.80			4.42		3.76				
24         C         0.67         0.95         0.91         3.50         4.76         4.64         4.02         5.95         3.61         1.96           25         C         0.69         0.95         0.98         3.54         4.76         4.63         4.024         5Hz         5.95         1.96           26         C         0.67         0.95         0.98         3.54         4.76         4.63         4.024         5Hz         2.98         3.61         1.96           28         M         0.72         0.99         0.98         3.56         4.43         3.775         3.08         3.61         1.96           29         M         0.71         0.96         0.98         3.56         4.44         3.775         3.03         3.60         2.03           30         M/W         0.77         0.98         0.89         3.56         4.44         4.04         4.054         5.Hz         4.054         5.Hz           31         C         0.72         0.89         0.83         3.60         5.24         4.64         4.04         4.054         5.Hz         3.00         3.65         3.05         3.03         3.05         3.03         3	24         C         0.67         0.95         0.91         3.50         4.76         4.63         4.02         5.95         1.97         1.97         2.03         2.05         2.03         2.04         2.02         2.02         2.04         1.96         2.02         2.04         1.96         1.96         2.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.04         4.024         4.04         4.034         4.034         4.034         4.034         4.034         4.034         4.034         4.034         4.034         4.034	24 C 0.67 0.95 0.91 3.50 4.76 4.64 4.02  25 C 0.69 0.95 0.98 3.54 4.76 4.63 4.02  28 C 0.69 0.95 0.98 3.54 4.76 4.63 4.02  28 M 0.72 0.98 0.98 3.50 4.76 4.63  29 M 0.71 0.96 0.98 3.56 4.44  30 M/W 0.70 0.90 0.89 3.56 5.24 4.64 4.04  31 C 0.72 0.89 0.89 3.56 5.24 4.64 4.04  32 C 0.73 0.89 0.89 3.56 5.23 4.20  33 C 0.77 0.92 0.86 5.03 5.03 5.23 4.20  34 C 0.77 0.92 0.86 7.00 5.20 4.65 5.23 4.20  35 M/W 0.77 0.92 0.86 7.00 5.20 4.65 5.23 4.20  36 C/M 0.77 0.92 0.86 7.00 7.00 7.00 7.00 7.00 7.00 7.00 7.0	M/M	0.68	0.94	0.95		3.82			4.47			3.00 3.56			
25         C         0.69         0.95         0.98         3.54         4.76         4.63         4.02         5 Hz         5.95         1.96           26         C         0.67         0.98         3.50         4.76         4.63         4.02         5 Hz         5.98         3.61         1.96           27         N         0.77         0.98         0.98         4.76         4.26         4.04         3.77s         3.03         3.60         1.96         1.96           29         M         0.71         0.96         0.98         3.56         4.43         3.77s         3.03         3.60         8.06         2.03           30         M/W         0.70         0.96         0.98         3.56         4.54         4.04         3.77s         3.03         3.60         8.06         2.03           31         C         0.72         0.89         0.89         3.56         5.24         4.64         4.04         4.05d         4.05d         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03	25         C         0.69         0.95         0.98         3.54         4.76         4.63         4.02d, 5Hz         4.02d, 5Hz         1.96         2.02         2.02           26         C         0.67         0.98         0.98         3.50         4.76         4.63         4.02d, 5Hz         2.98         3.61         1.96         2.01         2.02           28         M         0.74         0.97         0.98         3.50         4.76         4.26         4.02d, 5Hz         2.98         3.61         1.96         2.01         2.02           29         M         0.71         0.96         0.98         3.56         4.44         3.77s         3.03         3.60         1.96         1.96         1.98         1.99         1.90         1.9	25 C 0.69 0.95 0.98 3.54 4.76 4.63 4.02  26 C 0.67 0.95 0.93 3.50 4.76 4.63  27 M 0.72 0.98 0.98 3.50 4.76 4.63  28 M 0.74 0.97 0.97 3.56 4.43  30 M/W 0.70 0.96 0.98 3.56 5.24 4.64 4.04  31 C 0.75 0.88 0.89 3.56 5.24 4.64 4.04  32 C 0.77 0.92 0.86 3.60 5.23 4.20  33 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00  44 C 0.74 0.91 0.82 3.44 5.05 5.25 4.62  45 C 0.74 0.91 0.82 3.44 5.05 5.26 4.22  46 C/M 0.82 0.97 0.89 3.84 5.05 5.26 4.22  47 M 0.72 0.92 1.04 3.84 4.00 4.47  48 M 0.72 0.92 1.04 3.84 5.05 5.26 4.22  48 M/W 0.72 0.92 1.04 3.84 5.05 5.26 4.22  49 M/W 0.77 0.92 0.99 3.85  40 C 0.74 0.91 0.85 3.44 5.05 5.26 4.22  41 C 0.75 0.92 1.04 3.84 4.00 4.47  42 C 0.74 0.91 0.85 3.44 5.05 5.26 4.22  44 C 0.75 0.92 1.04 3.84 6.00 4.00 4.47  45 C 0.77 0.92 0.99 3.85  46 C/M 0.82 0.97 0.89 5.06 5.26 4.22  47 M 0.72 0.92 1.04 3.84 6.00 4.00 4.47  48 M/W 0.77 0.92 0.99 3.85  49 M/W 0.77 0.92 0.99 3.85  40 0.71 0.92 0.99 3.85  40 0.71 0.92 0.99 3.85  40 0.71 0.92 0.99 3.85  40 0.71 0.92 0.99 3.85  41 0.00 4.47  42 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.	၁	0.67	0.95	0.91	3.50		4.76		4.64	4.02					9 03
26         C         0.67         0.95         0.95         0.93         3.50         4.76         4.63         4.02d, 5 Hz         2.98 3.61         5.95         1.96           27         M         0.72         0.98         0.98         3.56         4.43         3.77s         2.98 3.61         5.95         1.96           29         M         0.71         0.96         0.98         3.56         4.44         3.77s         3.03 3.60         8.06         2.03           30         M/W         0.70         0.96         0.98         3.56         5.24         4.64         4.04         3.03 3.60         8.06         2.03           31         C         0.72         0.88         0.89         3.56         5.24         4.64         4.04<	26         C         0.67         0.98         0.98         4.76         4.63         4.02d, 5Hz         5.95         1.96         1.99         <	26 C 0.67 0.95 0.93 3.50 4.76 4.63 27 M 0.72 0.98 0.98 3.50 4.76 4.26 28 M 0.74 0.97 0.97 3.56 4.43 30 M/W 0.70 0.96 0.98 3.60 5.24 4.64 4.04 31 C 0.75 0.88 0.89 3.56 5.24 4.64 4.04 32 C 0.77 0.92 0.89 3.56 5.22 4.64 4.04 31 C 0.77 0.92 0.86 5.08 5.08 5.08 5.23 4.20 32 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00 44 C 0.74 0.91 0.82 3.44 5.05 5.25 4.62 45 C 0.77 0.92 0.97 0.89 3.84 4.00 4.47 48 M 0.72 0.92 1.04 3.84 4.00 4.47 49 M/W 0.77 0.92 0.99 3.84 5.05 5.26 4.22 47 M 0.77 0.92 0.90 3.44 5.05 5.26 4.22 48 M 0.72 0.92 1.04 3.84 4.00 4.47 49 M/W 0.71 0.92 0.99 3.84 5.06 5.26 4.22 40 0.74 0.91 0.85 3.44 5.05 5.26 4.22 41 C 0.74 0.91 0.85 3.44 5.05 5.26 4.22 42 C 0.74 0.91 0.85 3.44 5.05 5.26 4.22 44 C 0.77 0.92 0.93 1.03 3.84 4.00 4.47 49 M/W 0.77 0.92 0.99 3.84 4.00 4.47 40 0.72 0.92 1.04 3.84 4.00 4.47 40 0.72 0.92 1.04 3.84 6.00 4.47 40 0.74 0.91 0.85 3.44 5.05 5.26 4.22 40 m/W 0.71 0.92 0.99 3.85 40 0.74 0.91 0.85 3.44 5.05 5.26 4.22 41 0.72 0.92 1.04 3.84 4.00 4.47 42 0.74 0.91 0.85 3.44 5.05 5.26 4.22 43 0.74 0.91 0.85 3.44 5.05 5.26 4.22 44 0.07 0.72 0.93 1.03 3.82 3.98 4.43 45 0.77 0.92 0.99 3.85 3.84 4.00 4.47 47 0.77 0.92 0.99 3.84 4.00 4.47 48 m/W 0.77 0.92 0.99 3.85 3.84 4.00 4.47 49 m/W 0.71 0.92 0.99 3.85 3.84 4.00 4.47 40 0.75 0.90 1.00 1.00 1.00 1.00 1.00 1.00 1.00	ပ	0.69	0.95	0.98	3.54		4.76		4.63	4.02					9.6
27         M         0.72         0.98         0.98         4.76         4.26         4.26         4.26         4.26         4.43         3.77s         2.98 3.61         1.96         1.96           28         M         0.74         0.97         0.97         0.97         3.56         4.44         3.77s         3.03 3.60         8.06         2.08           30         M/W         0.75         0.89         0.89         3.56         5.24         4.64         4.04         8.06         2.03           34         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04         8.06         2.03           35         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04         4.04         8.06         2.03           36         C         0.77         0.92         0.86         3.56         4.22         4.64         4.04         4.04         4.05         3.00         3.01         3.03         3.01         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03         3.03 <td>27         M         0.72         0.98         0.98         4.76         4.26         2.98 3.61         1.96 1.98 1.99           28         M         0.72         0.98         0.98         3.56         4.43         3.775         3.03 3.60         8.06         2.03           30         M/W         0.70         0.96         0.96         3.56         4.44         3.775         3.03 3.60         8.06         2.03           31         C         0.72         0.88         0.89         3.56         5.24         4.64         4.05         <th< td=""><td>27       M       0.72       0.98       0.98       4.76       4.26         28       M       0.74       0.97       0.97       3.56       4.43         29       M       0.71       0.96       0.98       3.56       4.44         30       M/W       0.70       0.96       0.96       3.56       4.44         30       M/W       0.70       0.96       0.96       3.60       5.24       4.64       4.04         31       C       0.75       0.89       0.89       3.56       5.24       4.64       4.04         35       C       0.75       0.89       0.89       3.56       5.24       4.64       4.04         36       C/M       0.77       0.92       0.86       3.60       5.26       4.65       4.04         37       M       0.71       0.93       1.01       3.98       4.42       4.04         38       M/W       0.72       0.96       1.00       3.50       4.00       4.00       4.00         41       C       0.74       0.91       0.82       3.44       5.05       5.25       4.62       4.03         42       C       &lt;</td><td>၁</td><td>0.67</td><td>0.92</td><td>0.93</td><td>3.50</td><td></td><td>4.76</td><td></td><td>4.63</td><td></td><td></td><td></td><td>5,95</td><td></td><td>20.0</td></th<></td>	27         M         0.72         0.98         0.98         4.76         4.26         2.98 3.61         1.96 1.98 1.99           28         M         0.72         0.98         0.98         3.56         4.43         3.775         3.03 3.60         8.06         2.03           30         M/W         0.70         0.96         0.96         3.56         4.44         3.775         3.03 3.60         8.06         2.03           31         C         0.72         0.88         0.89         3.56         5.24         4.64         4.05 <th< td=""><td>27       M       0.72       0.98       0.98       4.76       4.26         28       M       0.74       0.97       0.97       3.56       4.43         29       M       0.71       0.96       0.98       3.56       4.44         30       M/W       0.70       0.96       0.96       3.56       4.44         30       M/W       0.70       0.96       0.96       3.60       5.24       4.64       4.04         31       C       0.75       0.89       0.89       3.56       5.24       4.64       4.04         35       C       0.75       0.89       0.89       3.56       5.24       4.64       4.04         36       C/M       0.77       0.92       0.86       3.60       5.26       4.65       4.04         37       M       0.71       0.93       1.01       3.98       4.42       4.04         38       M/W       0.72       0.96       1.00       3.50       4.00       4.00       4.00         41       C       0.74       0.91       0.82       3.44       5.05       5.25       4.62       4.03         42       C       &lt;</td><td>၁</td><td>0.67</td><td>0.92</td><td>0.93</td><td>3.50</td><td></td><td>4.76</td><td></td><td>4.63</td><td></td><td></td><td></td><td>5,95</td><td></td><td>20.0</td></th<>	27       M       0.72       0.98       0.98       4.76       4.26         28       M       0.74       0.97       0.97       3.56       4.43         29       M       0.71       0.96       0.98       3.56       4.44         30       M/W       0.70       0.96       0.96       3.56       4.44         30       M/W       0.70       0.96       0.96       3.60       5.24       4.64       4.04         31       C       0.75       0.89       0.89       3.56       5.24       4.64       4.04         35       C       0.75       0.89       0.89       3.56       5.24       4.64       4.04         36       C/M       0.77       0.92       0.86       3.60       5.26       4.65       4.04         37       M       0.71       0.93       1.01       3.98       4.42       4.04         38       M/W       0.72       0.96       1.00       3.50       4.00       4.00       4.00         41       C       0.74       0.91       0.82       3.44       5.05       5.25       4.62       4.03         42       C       <	၁	0.67	0.92	0.93	3.50		4.76		4.63				5,95		20.0
28         M         0.74         0.97         0.97         3.56         4.44         3.77s         3.03 3.60         8.06         2.03           29         M         0.71         0.96         0.98         3.56         4.44         3.77s         3.03 3.60         8.06         2.03           30         M/W         0.70         0.96         0.98         3.56         5.24         4.64         4.04         8.06         2.03           34         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04         8.06         2.02           35         C         0.77         0.99         0.89         3.56         5.24         4.64         4.04         4.054         5.95         8.06         2.02           36         C         M         0.77         0.93         1.00         4.07         4.04         4.05         4.05         8.13         2.02           37         M/W         0.72         0.96         1.00         4.00         4.00         4.00         4.00         4.00         4.00         4.00         4.00         4.00         4.00         4.00         4.00         4.00         4.00	28         M         0.74         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.97         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.98         0.99	28 M 0.74 0.97 0.97 3.56 4.43 3.0 M/W 0.71 0.96 0.98 3.56 4.44 3.0 M/W 0.70 0.96 0.96 3.56 4.44 3.1 C 0.72 0.88 0.80 3.60 5.24 4.64 4.04 3.2 C 0.73 0.89 0.83 3.60 5.22 4.65 4.65 3.2 C 0.73 0.89 0.83 3.60 5.23 4.20 3.7 M 0.71 0.93 1.01 3.98 4.42 3.8 M/W 0.72 0.96 1.00 4.07 4.07 4.57 3.9 M/W 0.72 0.96 1.00 5.23 4.00 4.50 4.1 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00 4.1 C 0.74 0.91 0.82 3.44 5.05 5.25 4.62 4.2 C 0.74 0.91 0.85 3.44 5.05 5.25 4.62 4.3 C 0.74 0.91 0.85 3.44 5.05 5.26 4.22 4.4 C 0.74 0.91 0.85 3.44 5.05 5.26 4.22 4.5 M 0.72 0.93 1.03 3.82 3.98 4.43 4.8 M 0.72 0.93 1.03 3.84 4.00 4.47 4.9 M/W 0.71 0.92 0.99 3.84 4.00 4.47 4.9 M/W 0.71 0.92 0.99 3.84 4.00 4.47 4.00 doublet, J=5-6 Hz. 5 doublet, J=6-10 Hz. 6 doublet, J=6-11 Hz. 7 d) triplet, J=6-11 Hz.	M	0.72	0.98	0.98			4.76		4.26			2.98 3.61	2		1 98 1 99
29         M         0.71         0.96         0.98         3.56         4.44         3.77s         3.03         3.60         8.06         2.03           30         M/W         0.70         0.96         0.98         3.56         4.44         3.77s         3.03         3.60         8.06         2.03           31         C         0.72         0.88         0.89         3.56         5.24         4.64         4.04         8.06         2.03           35         C         0.75         0.89         0.88         3.60         5.24         4.64         4.04         8.06         2.02           36         C/M         0.71         0.93         0.88         3.60         5.24         4.64         4.04         4.054         5.95         8.06         2.02           37         C         0.77         0.93         1.00         4.22         4.04         4.05         4.05         3.01	29         M         0.71         0.96         0.98         3.56         4.44         3.77s         3.03         3.60         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.66         2.03         3.03         3.69         2.03         3.03         3.69         2.03         3.03         3.60         2.03         3.03         3.69         2.03         3.03         3.03         3.03         3.69         2.03         3.0	<ul> <li>29 M 0.71 0.96 0.98 3.56 4.44</li> <li>30 M/W 0.70 0.96 0.96 3.60 3.56 4.52</li> <li>31 C 0.72 0.88 0.80 3.60 5.24 4.64 4.04</li> <li>34 C 0.75 0.89 0.89 3.56 5.22 4.64 4.04</li> <li>35 C 0.73 0.89 0.83 3.60 5.22 4.65 4.65 5.23 4.20</li> <li>36 C/M 0.77 0.92 0.86 5.23 4.20</li> <li>37 M 0.71 0.93 1.01 3.98 4.42</li> <li>38 M/W 0.72 0.96 1.00 4.07 4.00 4.50 4.00 4.50 4.00 4.50 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.03 4.03 4.03 4.03 5.20 4.60 4.03 0.93 3.50 4.03 5.26 4.22 4.64 4.04</li> <li>44 C 0.79 0.93 0.93 3.50 5.26 4.22 4.63 4.43 4.00 0.72 0.93 1.03 3.82 3.84 4.00 4.47 4.0 0.72 0.92 1.04 3.84 4.00 4.47</li> <li>45 C/M 0.72 0.93 1.03 3.84 4.00 4.47 4.00 4.47</li> <li>46 C/M 0.72 0.93 1.03 3.84 4.00 4.47</li> <li>47 M 0.72 0.92 1.04 3.84 4.00 4.47</li> <li>48 M/W 0.71 0.92 0.99 3.84 4.00 4.47</li> <li>49 M/W 0.71 0.92 0.99 3.84 4.00 4.47</li> <li>50 doublet, J=5-6 Hz.</li> <li>50 doublet, J=6-1Hz.</li> <li>50 doublet, J=6-7Hz.</li> </ul>	M	0.74	0.97	0.97			3.56		4.43						22.4
30         M/W         0.70         0.96         0.96         0.96         0.96         0.96         3.56         4.52         3.03         3.60         8.06         2.03           33         C         0.72         0.88         0.89         3.56         5.24         4.64         4.04         8.06         2.02           35         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04         8.06         2.02           36         C / M         0.77         0.92         0.89         3.56         5.24         4.64         4.04         4.054, 5 Hz         8.08         8.08         2.02           36         C / M         0.77         0.92         0.86         3.60         4.25         4.65         4.04         4.054, 5 Hz         3.00         3.62         8.08         8.08         2.02           37         M / W         0.77         0.92         0.97         4.07         4.57         3.80s         3.01         3.56         4.04         4.04         4.04         4.04         4.04         4.04         4.04         4.04         4.04         4.04         4.04         4.05         4.05         4.05	30         M/W         0.70         0.96         0.99         0.96         0.96         0.	30 M/W 0.70 0.96 0.96 3.56 4.52 33 C 0.72 0.88 0.80 3.60 5.24 4.64 4.04 34 C 0.75 0.89 0.89 3.56 5.24 4.64 4.04 35 C 0.73 0.89 0.83 3.60 5.22 4.65 36 C/M 0.77 0.92 0.86 5.23 4.20 37 M/V 0.72 0.96 1.00 4.07 4.07 4.00 4.50 39 M/W 0.72 0.96 1.00 4.00 4.00 4.00 4.60 44 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00 44 C 0.74 0.91 0.85 3.44 5.05 5.25 4.62 45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.62 46 C/M 0.82 0.97 0.89 5.06 5.26 4.22 47 M 0.72 0.93 1.03 3.84 4.00 4.47 48 M 0.72 0.93 1.04 3.84 4.00 4.47 49 M/W 0.71 0.92 0.99 3.84 50 C. M. 0.82 0.97 0.89 5.06 5.26 4.22 50 doublet, J=5−6 Hz. 50 doublet, J=5−6 Hz. 50 doublet, J=6−7 Hz. 51 C 0.74 0.91 0.85 3.84 52 C 0.74 0.91 0.85 3.84 53 C 0.74 0.91 0.85 3.84 50 C 0.74 0.91 0.80 50 C 0.74 0.91 0.91 50 C 0.74 0.91 0.80 50 C 0.74 0.91 50 C 0.74 0.91 0.91 50 C 0.74 0.91 0.80 50 C 0.74 0.91 50 C 0.74 0.91 0.80 50 C 0.74 0.91 50 C 0.7	M	0.71	0.96	0.98			3.56		4.44		3.77s				
33         C         0.72         0.88         0.80         3.60         5.24         4.64         4.04           34         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04           35         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04         4.04         8.08         2.02           36         C/M         0.77         0.92         0.86         3.60         5.24         4.64         4.04         4.05         5.04         8.08         2.04           37         M         0.77         0.92         0.86         1.01         3.98         4.42         3.80s         3.01         3.56         8.13         2.02           39         M/W         0.77         0.92         0.97         4.07         4.57         3.80s         3.01         3.56         8.06         8.10         2.02           44         C         0.74         0.91         0.82         3.44         5.05         5.25         4.60         4.00         4.03         4.03         8.14         8.14         8.14         8.14         8.14         8.14         8.14         8.	33         C         0.72         0.88         0.80         3.60         5.24         4.64         4.04           34         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04           35         C         0.77         0.89         0.89         3.56         5.24         4.64         4.04         8.06         2.02           36         C         0.77         0.92         0.88         3.60         5.24         4.64         4.04         8.06         2.04           37         C         0.77         0.92         0.86         3.08         3.00         3.62         3.00         3.62         3.04         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00         3.02         3.00	33 C 0.72 0.88 0.80 3.60 5.24 4.64 4.04 34 C 0.75 0.89 0.89 3.56 5.24 4.64 4.04 35 C 0.73 0.89 0.83 3.60 5.26 4.65 36 C/M 0.77 0.92 0.86 5.23 4.20 37 M 0.71 0.93 1.01 3.98 4.42 38 M/W 0.72 0.96 1.00 4.00 4.00 4.50 44 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00 44 C 0.79 0.93 0.93 3.50 4.63 4.63 4.63 45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.62 46 C/M 0.82 0.97 0.89 5.06 5.26 4.22 47 M 0.72 0.93 1.03 3.82 3.84 4.00 4.47 48 M 0.72 0.92 1.04 3.84 4.00 4.47 49 M/W 0.71 0.92 0.99 3.84 4.00 4.47 49 M/W 0.71 0.92 0.99 3.84 4.00 4.47 49 M/W 0.71 0.92 0.99 3.84	M/W	0.70	0.96	96.0			3.56		4.52			3.03 3.60			
34         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04           35         C         0.73         0.89         0.83         3.60         5.26         4.65         4.054         5Hz         5.95         8.08         2.02           36         C/M         0.77         0.92         0.86         3.98         4.42         3.00         3.62         8.13         2.02           37         M         0.71         0.93         1.01         4.07         4.27         3.80s         3.00         3.62         8.13         2.02           38         M/W         0.72         0.96         1.00         4.07         4.57         3.80s         3.01         3.56         8.06         8.10         2.02           43         C         0.74         0.91         0.82         3.44         5.03         5.22         4.60         4.00         4.03         4.03         8.06         8.10         8.06         8.10         8.06           43         C         0.74         0.91         0.82         3.44         5.05         5.25         4.62         4.03         4.03         4.03         4.03         4.	34         C         0.75         0.89         0.89         3.56         5.24         4.64         4.04         4.05d, 5 Hz         5.95         8.06         2.04           35         C         0.73         0.89         0.83         3.60         5.26         4.65         4.05d, 5 Hz         3.00         3.62         2.04           36         C/M         0.77         0.92         0.86         1.01         3.88         4.42         3.00         3.62         8.06         2.04           37         M         0.71         0.92         0.97         4.07         4.57         3.80s         3.01         3.69         8.06         2.02           49         C/M         0.72         0.99         3.44         5.03         5.22         4.60         4.00         4.03         8.06         8.10         2.03           45         C         0.74         0.91         0.85         3.44         5.05         5.25         4.63         4.03         4.03         4.43         3.01         3.64         8.06         8.06         2.04           45         C         0.74         0.91         0.85         3.44         5.05         5.25         4.63	34 C 0.75 0.89 0.89 3.56 5.24 4.64 4.04  35 C 0.73 0.89 0.83 3.60 5.26 4.65  36 C/M 0.77 0.92 0.86  37 M 0.71 0.93 1.01  38 M/W 0.72 0.96 1.00  44 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00  45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.63  46 C/M 0.82 0.97 0.89 5.06 5.26 4.22  47 M 0.72 0.93 1.03 3.82 3.84  48 M 0.72 0.93 1.03 3.84 4.00 4.77  4 0.01 0.85 3.44 5.05 5.25 4.63  48 M 0.72 0.92 1.04 3.84 4.00 4.47  49 M/W 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84  40 0.71 0.92 0.99 3.84	O	0.72	0.88	0.80	3.60			5.24	4.64	4.04		) 		8.06	2.03
35         C         0.73         0.89         0.83         3.60         5.26         4.65         4.05d, 5 Hz         5.95         8.06         2.04           36         C/M         0.77         0.92         0.86         4.20         3.98         4.42         3.00         3.62         8.06         2.04           37         M         0.71         0.92         0.86         1.01         4.07         4.57         3.80s         3.01         3.56         8.08         2.02           39         M/W         0.72         0.96         1.00         4.07         4.57         3.80s         3.01         3.56         8.06         8.10         2.03           44         C         0.74         0.91         0.82         3.44         5.05         5.22         4.60         4.03         4.03         4.03         4.03         8.08         8.15         2.06           45         C         0.74         0.91         0.85         3.44         5.05         5.25         4.62         4.03d	35         C         0.73         0.89         0.83         3.60         5.26         4.65         4.05d, 5 Hz         5.95         8.06         2.04           36         C/M         0.77         0.92         0.86         3.08         4.22         3.00         3.62         5.95         8.06         2.04           37         M         0.71         0.92         0.86         1.01         4.07         4.57         3.80s         3.01         3.56         2.02           49         M/W         0.72         0.92         0.97         0.82         3.44         5.03         5.25         4.60         4.00         4.03         4.03         8.06         8.10         2.03           44         C         0.79         0.93         3.50         3.44         5.05         5.25         4.62         4.03         5.95         8.10         8.16         2.04           45         C         0.74         0.91         0.83         3.82         3.84         4.00         4.47         3.80         3.00         3.56         8.14         8.14         8.14         8.20           46         C/M         0.82         0.97         0.89         3.84	35 C 0.73 0.89 0.83 3.60 5.26 4.65 36 C/M 0.77 0.92 0.86 5.23 4.20 37 M 0.71 0.93 1.01 3.98 4.42 38 M/W 0.72 0.96 1.00 4.07 4.07 4.57 39 M/W 0.70 0.92 0.97 4.00 4.50 44 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00 45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.63 4.63 4.03 46 C/M 0.82 0.97 0.89 5.06 5.26 4.22 47 M 0.72 0.93 1.03 3.82 3.84 4.00 4.47 48 M 0.72 0.92 1.04 3.84 4.00 4.47 49 M/W 0.71 0.92 0.99 3.84 4.00 4.47  a) C: CDCl <sub>8</sub> , M: CD <sub>8</sub> OD, W: D <sub>8</sub> O, D: d <sub>6</sub> -DMSO. b) doublet, J=5−4 Hz. c) doublet, J=6−7 Hz. d) triplet, J=6−7 Hz.	ر س	0.75	0.89	0.89	3.56			5.24	4.64	4.04				8.08	2.02.2.04
36         C/M         0.77         0.92         0.86         5.23         4.20         3.00         3.62         8.13         2.02           37         M         0.71         0.93         1.01         3.98         4.42         3.80s         3.00         3.62         8.13         2.02           39         M/W         0.72         0.96         1.00         4.07         4.57         3.80s         3.01         3.56         8.06         8.10         2.03           43         C         0.74         0.91         0.82         3.44         5.03         5.22         4.60         4.00         4.03         4.03         8.06         8.15         2.06           44         C         0.79         0.93         3.50         3.50         4.63         4.03         4.03         4.03         4.03         4.03         4.03         8.14         8.16         2.04           46         C/M         0.82         0.97         0.89         5.06         5.26         4.22         4.03         4.43         3.81         4.43         3.84         4.00         4.47         3.80           49         M/W         0.72         0.92         1.04 <t< td=""><td>36         C/M         0.77         0.92         0.86         5.23         4.20         3.00         3.62         8.13         2.02           37         M         0.71         0.93         1.01         3.98         4.42         3.80s         8.13         2.02           38         M/W         0.77         0.92         0.97         4.07         4.57         3.80s         3.01         3.56         8.06         8.10         2.02           44         C         0.74         0.91         0.82         3.44         5.03         5.22         4.60         4.00         4.63         4.03         8.06         8.10         8.14         8.14</td><td>36 C/M 0.77 0.92 0.86 5.23 4.20 37 M 0.71 0.93 1.01 3.98 4.42 38 M/W 0.72 0.96 1.00 4.07 4.57 39 M/W 0.70 0.92 0.97 4.00 4.50 44 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00 45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.63 46 C/M 0.82 0.97 0.89 5.06 5.26 4.22 47 M 0.72 0.93 1.03 3.82 3.98 4.43 48 M 0.72 0.92 1.04 3.84 4.00 4.47 49 M/W 0.71 0.92 0.99 3.84 4.00 4.47 a) C: CDCl<sub>8</sub>, M: CD<sub>8</sub>OD, W: D<sub>8</sub>O, D: d<sub>6</sub>-DMSO. b) doublet, J=5−6 Hz. c) doublet, J=6−7 Hz.</td><td><u>က</u></td><td>0.73</td><td>0.89</td><td>0.83</td><td>3.60</td><td></td><td></td><td>5.26</td><td>4.65</td><td></td><td></td><td></td><td>5.95</td><td>8.06</td><td>2.04 2.05</td></t<>	36         C/M         0.77         0.92         0.86         5.23         4.20         3.00         3.62         8.13         2.02           37         M         0.71         0.93         1.01         3.98         4.42         3.80s         8.13         2.02           38         M/W         0.77         0.92         0.97         4.07         4.57         3.80s         3.01         3.56         8.06         8.10         2.02           44         C         0.74         0.91         0.82         3.44         5.03         5.22         4.60         4.00         4.63         4.03         8.06         8.10         8.14         8.14	36 C/M 0.77 0.92 0.86 5.23 4.20 37 M 0.71 0.93 1.01 3.98 4.42 38 M/W 0.72 0.96 1.00 4.07 4.57 39 M/W 0.70 0.92 0.97 4.00 4.50 44 C 0.74 0.91 0.82 3.44 5.03 5.22 4.60 4.00 45 C 0.74 0.91 0.85 3.44 5.05 5.25 4.63 46 C/M 0.82 0.97 0.89 5.06 5.26 4.22 47 M 0.72 0.93 1.03 3.82 3.98 4.43 48 M 0.72 0.92 1.04 3.84 4.00 4.47 49 M/W 0.71 0.92 0.99 3.84 4.00 4.47 a) C: CDCl <sub>8</sub> , M: CD <sub>8</sub> OD, W: D <sub>8</sub> O, D: d <sub>6</sub> -DMSO. b) doublet, J=5−6 Hz. c) doublet, J=6−7 Hz.	<u>က</u>	0.73	0.89	0.83	3.60			5.26	4.65				5.95	8.06	2.04 2.05
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C/M	0.77	0.92	0.86				5.23	4.20			3.00 3.62	)	8.13	2.02 2.04
M/W       0.72       0.96       1.00       4.07       4.57       3.80s       3.01       3.56       8.06       8.10       2.03         M/W       0.70       0.92       0.97       4.00       4.50       4.00       4.00       8.06       8.10       8.06       8.10       2.03         C       0.74       0.91       0.85       3.44       5.03       5.25       4.60       4.00       8.08       8.15       2.06         C       0.74       0.91       0.85       3.44       5.05       5.25       4.62       4.034       5.95       8.10       8.16       2.04         C/M       0.82       0.97       0.89       5.06       5.26       4.22       3.01       3.64       8.14       8.20       2.04         M       0.72       0.93       1.03       3.84       4.00       4.47       3.80         M/W       0.72       0.92       1.04       3.84       4.00       4.47       3.80	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	X.	0.71	0.93	1.01				3.98	4.42					) (	
M/W       0.70       0.92       0.97       4.00       4.50       3.01       3.56       8.06       8.10       2.03         C       0.74       0.91       0.82       3.44       5.03       5.22       4.60       4.00         C       0.79       0.93       0.93       3.50       4.63       4.03       8.08       8.15       2.06         C       0.74       0.91       0.85       3.44       5.05       5.25       4.62       4.034       5.14       8.10       8.16       2.04         C/M       0.82       0.97       0.89       5.06       5.26       4.22       3.01       3.64       8.14       8.20       2.04         M       0.72       0.93       1.03       3.82       3.98       4.43       3.80         M/W       0.72       0.92       1.04       3.84       4.00       4.47       3.80	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	M/W	0.72	0.96	1.00				4.07	4.57		3.80s				
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C 0.79 0.93 0.93 3.50 4.63 4.03 8.08 8.15 2.06 C 0.74 0.91 0.85 3.44 5.05 5.25 4.62 4.03 4.03d, 5 Hz 5.95 8.10 8.16 2.04 C/M 0.82 0.97 0.89 5.06 5.26 4.22 3.98 4.43 3.82 3.98 4.47 3.80 M.W. 0.72 0.92 1.04 3.84 4.00 4.47 3.80	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	ပ	0.74	0.91	0.82	3.44	0.		5.22	4.60	4.00				8.06.8.10	2.03 2.04
C 0.74 0.91 0.85 3.44 5.05 5.25 4.62 4.03d, 5 Hz 5.95 8.10 8.16 2.04 C/M 0.82 0.97 0.89 5.06 5.26 4.22 3.01 3.64 8.14 8.20 2.04 M 0.72 0.93 1.03 3.82 3.98 4.43 3.80 M W 0.72 0.92 1.04 3.84 4.00 4.47 3.80	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	<u>ن</u>	0.79	0.93	0.93	3.50				4.63	4.03				8.08 8.15	2.06
C/M 0.82 0.97 0.89 5.06 5.26 4.22 3.01 3.64 8.14 8.20 2.04 M 0.72 0.93 1.03 3.82 3.98 4.43 3.80 M 0.72 0.92 1.04 3.84 4.00 4.47 3.80	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	ပ	0.74	0.91	0.85	3.44	5.05		5.25	4.62				5,95	8 10 8 16	2.04.2.05
M 0.72 0.93 1.03 3.82 3.98 4.43 M 0.72 0.92 1.04 3.84 4.00 4.47 3.80 M/W 0.71 0.92 0.93	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	M 0.72 0.93 1.03 3.82 3.98 4.43 M 0.72 0.92 1.04 3.84 4.00 4.47 M/W 0.71 0.92 0.99 3.84 4.00 4.47 a) C: CDCl <sub>8</sub> , M: CD <sub>8</sub> OD, W: D <sub>8</sub> O, D: $d_{o}$ -DMSO. b) doublet, $J = 5 - 6$ Hz. c) doublet, $J = 6 - 7$ Hz.	$^{\rm C/M}$	0.82	0.97	0.89		5.06		5.26	4.22			3.01 3.64		8.14.8.20	2.04 2.06
M 0.72 0.92 1.04 3.84 4.00 4.47 3.80 M/W 0.71 0.92 0.90 9.94	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	M 0.72 0.92 1.04 3.84 4.00 4.47 M/W 0.71 0.92 0.99 3.84 4.00 4.47 a) C: CDCl <sub>8</sub> , M: CD <sub>8</sub> OD, W: D <sub>8</sub> O, D: $d_{o}$ -DMSO. b) doublet, $J = 5 - 6$ Hz. c) doublet, $J = 7 - 10$ Hz. d) triplet, $J = 6 - 7$ Hz.	$\mathbb{X}$	0.72	0.93	1.03		3.82		3.98	4.43			•		1	
M/W 0.71 0.99 0.99 9.94 4.00 1.77	M/W 0.71 0.92 0.99 3.84 4.00 4.47 3.00 a) C: CDCl <sub>3</sub> , M: CD <sub>3</sub> OD, W: D <sub>2</sub> O, D: $d_{a}$ -DMSO. b) doublet, $J = 5 - 6$ Hz. c) doublet, $J = 7 - 10$ Hz.	M/W 0.71 0.92 0.99 3.84 4.00 4.47 a) C: CDCl <sub>8</sub> , M: CD <sub>8</sub> OD, W: D <sub>8</sub> O, D: $d_a$ -DMSO. b) doublet, $J = 5 - 6$ Hz. c) doublet, $J = 7 - 10$ Hz. d) triplet, $J = 6 - 7$ Hz.	M	0.72	0.92	1.04		3.84		4.00	4.47		3.80				
3.00	C: CDCl <sub>3</sub> , M: CD <sub>3</sub> OD, W: D <sub>2</sub> O, D: $d_0$ -D doublet, $J = 5 - 6$ Hz. doublet, $J = 7 - 10$ Hz.	C: CDCl <sub>8</sub> , M: CD <sub>3</sub> OD, W: D <sub>2</sub> O, D: $d_0$ -L doublet, $J = 5 - 6$ Hz. doublet, $J = 7 - 10$ Hz. triplet, $J = 6 - 7$ Hz.	M/M	0.71	0.92	0.99		3.84		4.00	4.47			3.00 3.56			
					CDCl <sub>8</sub> , M: blet, $J = 5$	CD <sub>8</sub> OD, W —6 Hz.	V: D <sub>2</sub> O, D;	: d <sub>o</sub> -DMSC	ċ.								
C: CDCl <sub>3</sub> , M: CD <sub>3</sub> OD, W: D <sub>2</sub> O, D: $d_0$ -D doublet, $J = 5 - 6$ Hz.					blet, $J = 7$ .	—10 Hz.											

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indicating a trans-diaxial relationship to the vicinal 2'-proton. Further evidence for the  $\beta$ -glucoside linkage in these monoglucuronides was obtained by characterizing the bile acid liberated after incubation with the  $\beta$ -glucuronidase preparation.

The NMR spectral data for 3-glucuronides of various bile acids and their derivatives are collected in Table I. The availability of these data may be helpful for the characterization of bile acids and related compounds.

Studies on the chromatographic separation of 3-glucuronides of unconjugated and conjugated bile acids are being conducted in these laboratories and the details will be reported elsewhere in the near future.

## Experimental<sup>11)</sup>

General Procedure for the Preparation of 3- $\beta$ -p-Glucopyranuronoside (Glucuronide) ——Freshly prepared CdCO<sub>3</sub> (800 mg) and methyl 1-bromo-1-deoxy-2,3,4-tri-O-acetyl- $\beta$ -p-glucopyranuronate (500 mg) were added to a solution of bile acid (0.001 mol) in anhydrous toluene or benzene (24 ml) and the suspension was azeotropically distilled with stirring over a period of 1.5 hr. Additional portion of the acetobromosugar (300 mg) and CdCO<sub>3</sub> (500 mg) were added and the solution was refluxed for another 1.5 hr. The precipitate was removed by filtration and washed with toluene or benzene. The filtrate and washings were combined and evaporated down *in vacuo*. The oily residue was subjected to column chromatography on silica gel (20 g). Elution with hexane–AcOEt and recrystallization of the eluate gave the glucuronide acetate–methyl ester.

Methyl Lithocholate 3-Glucuronide Acetate-Methyl Ester (4)—Methyl lithocholate (2) (490 mg) was subjected to glucuronidation by means of the Koenigs-Knorr reaction in toluene. Recrystallization of the crude product from acetone–hexane gave 4 (121 mg) as colorless needles. mp 175—176°. [ $\alpha$ ] $_{\rm D}^{25}$  -26.9° (c=0.1, CHCl $_{\rm 3}$ ). Anal. Calcd for C $_{\rm 38}$ H $_{\rm 58}$ O $_{\rm 12}$ ·1/2H $_{\rm 2}$ O: C, 63.73; H, 8.31. Found: C, 64.01; H, 8.38.

Lithocholic Acid 3-Glucuronide Disodium Salt (9)—NaOH solution (7%, 30 ml) was added to a solution of 4 (85 mg) in MeOH (70 ml) and the mixture was stirred at 40° for 32 hr. The resulting solution was poured into ice-water, neutralized with conc. HCl and evaporated down in vacuo. The residue obtained was dissolved in 2% NaOH (55 ml) and subjected to column chromatography on Amberlite XAD-2. The eluate was redissolved in  $H_2O$  (20 ml) and subjected to ion-exchange chromatography on Dowex-50W-X8 (Na<sup>+</sup> form). Recrystallization of the eluate from  $H_2O$ -MeOH-acetone gave 9 (43 mg) as a colorless amorphous substance. mp 257—259° (dec.). [ $\alpha$ ]<sup>25</sup> = 10.3° (c=0.1,  $H_2O$ ). Anal. Calcd for  $C_{30}H_{34}Na_2O_9 \cdot 2H_2O$ : C, 56.95; H, 7.96. Found: C, 56.60; H, 7.55.

Ethyl Glycolithocholate 3-Glucuronide Acetate-Methyl Ester (7)—i) p-Nitrophenyl lithocholate (3)<sup>5</sup>) (700 mg) was subjected to glucuronidation by means of the Koenigs-Knorr reaction in toluene. Recrystallization of the crude product from acetone-bexane gave p-nitrophenyl lithocholate 3-glucuronide acetate-methyl ester (6) (262 mg) as colorless needles. mp 187—187.5°. Ethyl glycinate (50 mg) in pyridine (1 ml) was added to a solution of 6 (120 mg) in pyridine (3 ml) and the solution was stirred at room temperature for 1 hr. The reaction mixture was poured into ice-water, acidified with 5% HCl and extracted with AcOEt. The organic layer was washed with H<sub>2</sub>O, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated down *in vacuo*. The oily residue was subjected to column chromatography on silica gel (6 g). Elution with hexane–AcOEt and recrystallization of the eluate from acetone–hexane gave 7 (99 mg) as colorless needles. mp 170—171°. [ $\alpha$ ]<sup>25</sup>  $_{\rm c}$  –21.8° (c=0.1, CHCl<sub>3</sub>). Anal. Calcd for C<sub>41</sub>H<sub>63</sub>NO<sub>13</sub>: C, 63.30; H, 8.16; N, 1.80. Found: C, 63.42; H, 8.31; N, 2.15.

ii) Lithocholic acid (1) (500 mg) was subjected to glucuronidation by means of the Koenigs-Knorr reaction in toluene. Recrystallization of the crude product from acetone-hexane gave lithocholic acid 3-glucuronide acetate-methyl ester (5) (492 mg) as colorless needles. mp 170°. p-Nitrophenol (110 mg) and N,N'-dicyclohexylcarbodiimide (190 mg) in anhydrous AcOEt (7 ml) were added to a solution of 5 (235 mg) in anhydrous AcOEt (7 ml)-dioxane (6 ml) and the solution was stirred at room temperature for 7.5 hr. After removal of the precipitate by filtration, the filtrate was evaporated down in vacuo. The oily residue was chromatographed on silica gel (15 g). Elution with hexane-AcOEt (5:1—3:1) gave 6 (139 mg) as colorless needles. Treatment of 6 with ethyl glycinate as described in i) gave 7. mp 170—171°. Mixed melting point determination after admixture with the sample obtained in i) showed no depression.

Glycolithocholic Acid 3-Glucuronide Disodium Salt (10)—NaOH solution (20%, 3 ml) was added to a solution of 7 (100 mg) in H<sub>2</sub>O (300 ml) and the solution was stirred at 40° for 15 hr. The reaction mixture was subjected to column chromatography on Amberlite XAD-2 and then to ion-exchange chromatography on Dowex-50W-X8 (Na<sup>+</sup> form). Recrystallization of the eluate from H<sub>2</sub>O-MeOH-acetone gave 10 (55 mg)

<sup>11)</sup> All melting points were taken on a micro hot-stage apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 polarimeter. NMR spectra were recorded on a JEOL PS-100 spectrometer at 100 MHz using tetramethylsilane or sodium 2,2-dimethyl-2-silapentane-5-sulfonate as an internal standard.

as a colorless amorphous substance. mp 253—256° (dec.).  $[\alpha]_D^{25}$  —19.2° ( $\varepsilon$ =0.1, H<sub>2</sub>O). Anal. Calcd for  $C_{32}H_{49}NNa_2O_{10}\cdot 21/2H_2O$ : C, 55.00; H, 7.79; N, 2.00. Found: C, 55.07; H, 7.86; N, 1.88.

Taurolithocholic Acid 3-Glucuronide Disodium Salt (11)—Taurine (63 mg) in  $\rm H_2O$  (5.5 ml) was added to a solution of 6 (250 mg) in pyridine (22 ml) and the mixture was stirred at room temperature for 6 hr. The resulting solution was concentrated and the oily residue was chromatographed on silica gel (10 g). Elution with CHCl<sub>3</sub>-MeOH (5: 1—2: 1) gave taurolithocholate 3-glucuronide acetate-methyl ester (8) (136 mg) as an oily product. Aq. NH<sub>4</sub>OH (28%, 12 ml) was added to a solution of 8 (40 mg) in MeOH (16 ml) and the mixture was stirred at 37° for 2 days. The resulting solution was evaporated down in vacuo and the residue was dissolved in MeOH (40 ml). After addition of 20% NaOH (2 ml) the solution was stirred at room temperature overnight. The resulting solution was concentrated and the precipitate was collected by filtration. The precipitate was dissolved in 72% EtOH (15 ml) and subjected to ion-exchange chromatography on Amberlyst A-15 (H+ form). The eluate was rechromatographed on Amberlyst A-15 (Na+ form). Recrystallization of the eluate from  $\rm H_2O-MeOH-ether$  gave 11 (10 mg) as a pale brown amorphous substance. mp 263—266° (dec.). [ $\alpha$ ] $_{\rm D}^{25}$  -32.6° (c=0.1, 80% EtOH). Anal. Calcd for  $\rm C_{32}H_{51}NNa_2O_{11}S\cdot 2H_2O$ : C, 51.95; H, 7.88; N, 1.89. Found: C, 51.64; H, 7.82; N, 2.32.

Methyl 7-Formylchenodeoxycholate 3-Glucuronide Acetate-Methyl Ester (15)—Treatment of methyl 7-formylchenodeoxycholate (13) (700 mg) as described for 4 followed by recrystallization from acetone-hexane gave 15 (273 mg) as colorless needles. mp 209.5—210.5°.  $[\alpha]_D^{25}$  —12.4° (c=0.1, CHCl<sub>3</sub>). Anal. Calcd for  $C_{39}H_{58}O_{14}$ : C, 62.38; H, 7.79. Found: C, 62.59; H, 7.74.

Chenodeoxycholic Acid 3-Glucuronide Disodium Salt (19)—Treatment of 15 (100 mg) as described for 9 followed by recrystallization from MeOH-ether gave 19 (50 mg) as a colorless amorphous substance. mp 261—263° (dec.).  $[\alpha]_D^{25} - 10.4^\circ$  (c = 0.1, MeOH). Anal. Calcd for  $C_{30}H_{34}Na_2O_{10} \cdot H_2O$ : C, 57.13; H, 7.67. Found: C, 57.25; H, 8.00.

Ethyl 7-Formylglycochenodeoxycholate 3-Glucuronide Acetate-Methyl Ester (17)——i) Treatment of 7-formylchenodeoxycholic acid<sup>5,12)</sup> (12) (223 mg) as described for 7-i) followed by recrystallization from acetone—hexane gave 17 (32 mg) as colorless needles. mp 217—219°. [ $\alpha$ ]<sup>25</sup> — 9.6° (c=0.1, CHCl<sub>3</sub>). Anal. Calcd for C<sub>42</sub>H<sub>63</sub>NO<sub>15</sub>: C, 61.37; H, 7.73; N, 1.70. Found: C, 61.23; H, 7.76; N, 2.00. ii) Treatment of 12 (1.49 g) as described for 7-ii) followed by recrystallization from acetone-hexane

- ii) Treatment of 12 (1.49 g) as described for 7-ii) followed by recrystallization from acetone-hexane gave 17 (178 mg) as colorless crystals. mp 217—219°. Mixed melting point determination after admixture with the sample obtained in i) showed no depression.
- iii) Ethyl 7-formylglycochenodeoxycholate (14) (500 mg) was subjected to glucuronidation by means of the Koenigs-Knorr reaction in benzene to give 17 (128 mg) as colorless needles. mp 216—219°. Mixed melting point determination after admixture with the sample obtained in i) showed no depression.

Glycochenodeoxycholic Acid 3-Glucuronide Disodium Salt (20)——Treatment of 17 (100 mg) as described for 19 followed by recrystallization from MeOH-ether gave 20 (50 mg) as a colorless amorphous substance. mp 255—259° (dec.). [ $\alpha$ ]<sup>25</sup> -8.2° (c=0.1, MeOH). Anal. Calcd for C<sub>32</sub>H<sub>49</sub>NNa<sub>2</sub>O<sub>11</sub>·11/2H<sub>2</sub>O: C, 55.16; H, 7.52; N, 2.01. Found: C, 55.26; H, 7.25; N, 1.98.

Taurochenodeoxycholic Acid 3-Glucuronide Dipotassium Salt (21)——p-Nitrophenyl 7-formylchenodeoxycholate 3-glucuronide acetate-methyl ester (16) (70 mg) was condensed with taurine as described above to give 7-formyltaurochenodeoxycholate 3-glucuronide acetate-methyl ester (18) (36 mg) as an oily product. KOH solution (10%, 20 ml) was added to a solution of 18 (50 mg) in MeOH (30 ml) and the mixture was stirred at 40° for 2 days. The resulting solution was poured into ice-water, neutralized with conc. HCl and evaporated down in vacuo. The residue was dissolved in 3% KOH (70 ml) and subjected to column chromatography on Amberlite XAD-2. The eluate was redissolved in  $H_2O$  (10 ml) and subjected to ion-exchange chromatography on Dowex-50W-X8 (K+ form). Recrystallization of the eluate from aq. acetone gave 21 (29 mg) as colorless needles. mp 281—284° (dec.).  $\alpha_1^{-1} + 11.0^{\circ}$  ( $\alpha_2^{-1} + 11.0^{\circ}$ ). Anal. Calcd for  $C_{32}H_{51}K_2-NO_{12}S\cdot H_2O$ : C, 49.91; H, 6.94; N, 1.82. Found: C, 49.59; H, 7.24; N, 1.78.

Methyl 7-Acetylursodeoxycholate 3-Glucuronide Acetate-Methyl Ester (24) — Methyl 7-acetylursodeoxycholate (22)<sup>5)</sup> (400 mg) was subjected to glucuronidation by means of the Koenigs-Knorr reaction in toluene. The oily residue was subjected to column chromatography on silica gel (25 g). Elution with benzene-ether (10: 1—6: 1) and recrystallization of the eluate from hexane-ether gave 24 (182 mg) as colorless needles. mp 161—162°. [ $\alpha$ ]<sup>25</sup> + 3.8° (c=0.1, CHCl<sub>3</sub>). Anal. Calcd for C<sub>40</sub>H<sub>60</sub>O<sub>14</sub>: C, 62.81; H, 7.91. Found: C, 62.72; H, 7.63.

Ursodeoxycholic Acid 3-Glucuronide Disodium Salt (28)——Treatment of 24 (100 mg) as described for 9 followed by recrystallization from MeOH-ether gave 28 (50 mg) as a colorless amorphous substance. mp 264—268° (dec.).  $[\alpha]_0^{25} + 3.8^\circ$  (c=0.1, MeOH). Anal. Calcd for  $C_{30}H_{46}Na_2O_{10}\cdot 1/2H_2O$ : C, 57.96; H, 7.62. Found: C, 57.86; H, 7.81.

Ethyl 7-Acetylglycoursodeoxycholate 3-Glucuronide Acetate-Methyl Ester (26)——Treatment of 7-acetylursodeoxycholic acid (23)<sup>5)</sup> (360 mg) as described for 7-i) followed by recrystallization from ether gave 26 (31 mg) as a colorless amorphous substance. mp 118—123°. [ $\alpha$ ]<sup>25</sup> +6.0° (c=0.1, CHCl<sub>3</sub>). Anal. Calcd

<sup>12)</sup> K.-Y. Tserng and P.D. Klein, Steroids, 29, 635 (1977).

for C<sub>43</sub>H<sub>65</sub>NO<sub>15</sub>: C, 61.78; H, 7.84; N, 1.67. Found: C, 61.68; H, 7.63; N, 1.58.

Glycoursodeoxycholic Acid 3-Glucuronide Disodium Salt (29)—Treatment of 26 (75 mg) as described for 9 followed by recrystallization from MeOH-ether gave 29 (38 mg) as a colorless amorphous substance. mp  $250-253^{\circ}$  (dec.). [ $\alpha$ ]<sup>25</sup>  $+6.1^{\circ}$  (c=0.1, MeOH). Anal. Calcd for  $C_{32}H_{49}NNa_2O_{11}\cdot11/2H_2O$ : C, 55.16; H, 7.52; N, 2.01. Found: C, 55.15; H, 7.69; N, 1.80.

Tauroursodeoxycholic Acid 3-Glucuronide Dipotassium Salt (30)—Treatment of p-nitrophenyl 7-acetylursodeoxycholate 3-glucuronide acetate-methyl ester (25) (120 mg) as described for 21 gave 30 (43 mg) as a colorless amorphous substance. mp 250—253° (dec.). [ $\alpha$ ]<sub>25</sub> +21.1° (c=0.1, H<sub>2</sub>O). Anal. Calcd for  $C_{32}H_{51}K_2NO_{12}S \cdot 1/2H_2O$ : C, 50.50; H, 6.76; N, 1.84. Found: C, 50.48; H, 7.22; N, 1.46.

Methyl 12-Formyldeoxycholate 3-Glucuronide Acetate-Methyl Ester (33)—Methyl 12-formyldeoxycholate (32)<sup>5,12)</sup> (400 mg) was subjected to glucuronidation in toluene as described for 4 to give 33 (292 mg) as colorless needles. mp 211°. [ $\alpha$ ]<sub>D</sub><sup>25</sup> +36.5° (c=0.1, CHCl<sub>3</sub>). Anal. Calcd for C<sub>39</sub>H<sub>58</sub>O<sub>14</sub>: C, 62.38; H, 7.79. Found: C, 62.47; H, 7.97.

Deoxycholic Acid 3-Glucuronide Disodium Salt (37)—Treatment of 33 (100 mg) as described for 10 followed by recrystallization from MeOH-ether gave 37 (45 mg) as a pale yellow amorphous substance. mp 264— $267^{\circ}$  (dec.). [ $\alpha$ ]<sub>D</sub><sup>25</sup> +15.7° (c=0.1, MeOH). Anal. Calcd for  $C_{30}H_{34}O_{10}Na_2 \cdot 1/2H_2O$ : C, 57.96; H, 7.62. Found: C, 57.84; H, 7.82.

Ethyl 12-Formylglycodeoxycholate 3-Glucuronide Acetate-Methyl Ester (35)—i) Treatment of 12-formyldeoxycholic acid (31) (270 mg) as described for 7-i) followed by recrystallization from hexane-AcOEt gave 35 (32 mg) as a colorless amorphous substance. mp 141—144°. [ $\alpha$ ] $_{\rm D}^{25}$  +20.8° (c=0.1, CHCl $_{\rm 3}$ ). Anal. Calcd for C $_{42}$ H $_{63}$ NO $_{15}$ ·H $_{2}$ O: C, 60.05; H, 7.80; N, 1.67. Found: C, 60.39; H, 7.56; N, 1.46.

ii) Treatment of 31 (1.5 g) as described for 7-ii) followed by recrystallization from hexane-AcOEt gave 35 (138 mg). mp 141—144°. Mixed melting point determination after admixture with the sample obtained in i) showed no depression.

Glycodeoxycholic Acid 3-Glucuronide Disodium Salt (38)—Treatment of 35 (100 mg) as described for 9 followed by recrystallization from aq. MeOH gave 38 (30 mg) as a colorless amorphous substance. mp  $252-255^{\circ}$  (dec.). [ $\alpha$ ]<sup>25</sup> +18.9° (c=0.1, H<sub>2</sub>O). Anal. Calcd for C<sub>32</sub>H<sub>49</sub>NNa<sub>2</sub>O<sub>11</sub>·2H<sub>2</sub>O: C, 54.46; H, 7.57; N, 1.98. Found: C, 54.27; H, 7.57; N, 1.96.

Taurodeoxycholic Acid 3-Glucuronide Dipotassium Salt (39)—Treatment of p-nitrophenyl 12-formyldeoxycholate 3-glucuronide acetate-methyl ester (34) (160 mg) as described for 21 followed by recrystallization from aq. MeOH gave 39 (38 mg) as colorless needles. mp 282—285° (dec.). [ $\alpha$ ]<sup>25</sup> +31.3° (c=0.1, H<sub>2</sub>O). Anal. Calcd for C<sub>32</sub>H<sub>51</sub>K<sub>2</sub>NO<sub>12</sub>S·2H<sub>2</sub>O: C, 48.77; H, 7.04; N, 1.78. Found: C, 49.11, H, 7.11; N, 1.25.

Methyl 7,12-Diformylcholate 3-Glucuronide Acetate-Methyl Ester (43)—Treatment of methyl 7,12-diformylcholate (41)<sup>5,12)</sup> (390 mg) as described for 4 followed by recrystallization from hexane-AcOEt gave 43 (227 mg) as colorless needles. mp 232—233°. [ $\alpha$ ]<sup>25</sup> +20.8° (c=0.1, CHCl<sub>3</sub>). Anal. Calcd for C<sub>40</sub>H<sub>58</sub>O<sub>16</sub>·1/2H<sub>2</sub>O: C, 59.17; H, 7.33. Found: C, 59.46; H, 7.30.

Cholic Acid 3-Glucuronide Disodium Salt (47)——Treatment of 43 (100 mg) as described for 9 followed by recrystallization from MeOH–ether gave 47 (44 mg) as a pale yellow amorphous substance. mp 269—272° (dec.).  $[\alpha]_{2}^{25} + 3.8^{\circ}$  (c = 0.1, MeOH). Anal. Calcd for  $C_{30}H_{34}Na_{2}O_{11} \cdot 11/2 H_{2}O$ : C, 54.95; H, 7.53. Found: C, 54.80; H, 7.93.

Ethyl 7,12-Diformylglycocholate 3-Glucuronide Acetate-Methyl Ester (45)——i) Treatment of 7,12-diformylcholic acid (40) (130 mg) as described for 7-i) followed by recrystallization from hexane-AcOEt gave 45 (18 mg) as colorless needles. mp 200—203°. [ $\alpha$ ] $_{\rm p}^{15}$  +24.0° (c=0.1, CHCl $_{\rm s}$ ). Anal. Calcd for C $_{\rm 43}$ H $_{\rm 63}$ NO $_{\rm 17}$ · H $_{\rm 2}$ O: C, 58.42; H, 7.41; N, 1.58. Found: C, 58.67; H, 7.59; N, 1.85.

ii) Treatment of 40 (360 mg) as described for 7-ii) followed by recrystallization from hexane-AcOEt gave 45 (33 mg) as colorless needles. mp 199—201°. Mixed melting point determination after admixture with the sample obtained in i) showed no depression

iii) Ethyl 7,12-diformylglycocholate (42)<sup>5)</sup> (730 mg) was subjected to glucuronidation by means of the Koenigs-Knorr reaction in benzene to give 45 (45 mg) as colorless needles. mp 198—200°. Mixed melting point determination after admixture with the sample obtained in i) showed no depression.

Glycocholic Acid 3-Glucuronide Disodium Salt (48)—Treatment of 45 (60 mg) as described for 9 followed by recrystallization from MeOH-ether gave 48 (20 mg) as a colorless amorphous substance. mp 257—260° (dec.).  $[\alpha]_D^{25}$  -6.1° (c=0.1, MeOH). Anal. Calcd for  $C_{32}H_{49}NNa_2O_{12}\cdot H_2O$ : C, 54.61; H, 7.31; N, 1.99. Found: C, 54.79; H, 7.15; N, 2.04.

Taurocholic Acid 3-Glucuronide Dipotassium Salt (49)—Treatment of p-nitrophenyl 7,12-diformylcholate 3-glucuronide acetate-methyl ester (44) (250 mg) as described for 21 followed by recrystallization from aq. acetone gave 49 (20 mg) as colorless plates. mp 246—250° (dec.). [ $\alpha$ ]<sub>p</sub> +10.0° (c=0.1, H<sub>p</sub>O). Anal. Calcd for  $C_{32}H_{51}K_{2}NO_{13}S\cdot 11/2H_{2}O$ : C, 48.34; H, 6.85; N, 1.76. Found: C, 48.26; H, 7.06; N, 1.72.

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